Remarks

Claims 1-42 and 44-52 are currently pending. Claim 42 is currently amended.

Claim Rejections – 35 USC § 112

Claims 42, 44-48, and 52 stand rejected under 35 USC § 112, first paragraph, as failing to comply with the written description requirement. Claim 42 is currently amended to recite "dispersed shear deformable particles of a self-crosslinking polymer." Support for this amendment may be found on page 2, lines 13-14. Claims 44-48 and 52 are dependent on claim 42. Applicant respectfully requests withdrawal of this rejection.

Claim Rejections – 35 USC § 103 – Kubota et al. in view of Krepski et al.

Prior art references do not teach or suggest all the claim limitations

Claims 1-2, 4, 6-9, 15-27, 34-42, 44-49, and 51-52 stand rejected under 35 USC § 103(a) as being unpatentable over Kubota et al. (US 5,846,306) in view of Krepski et al. (US 5,929,160). The Examiner states, in the Office Action of August 21, 2003, that Kubota et al. disclose an ink jet ink comprising aqueous vehicle, pigment, humectant, acrylic resin, and 0.1-40 wt. % polyurethane. The Examiner also states, in the Office Action dated November 26, 2004, that Kubota et al. disclose "the use of generic type of polymer, i.e., polyurethane".

Applicant has not found support for either of these statements in Kubota et al., and thus it is assumed that the Examiner has constructed it from various, i.e., separate, parts of the disclosure. More accurately, Kubota et al. disclose that 0.1 to 40 wt. % of a resin emulsion may be incorporated into the ink of their invention (col. 6, lines 64-67), that the resin emulsion may be a thermoplastic resin (col. 7, lines 9-11), and that a polyurethane may be used as a water-insoluble thermoplastic resin (col. 7, lines 28-29 and 42). Thus, Kubota et al. disclose the use of a particular type of polyurethane in ink jet inks: those that are water-insoluble and thermoplastic.

The polyurethanes disclosed in Kubota et al. are very different from the ones of the present invention; one difference is that they are thermoplastic and thermoset, respectively. The

following exerpt is taken from page 1141 of "Hawley's Condensed Chemical Dictionary", 12th Ed. by R.J. Lewis, Sr., published by Van Nostrand Reinhold Co., 1993: A thermoplastic polymer is a polymer "that softens when exposed to heat and returns to its original condition when cooled to room temperature." Thermoplastic properties of the polyurethanes that Kubota et al. are using are critical to the performance of their inks, hence the disclosure on softening temperatures, glass transition temperatures , minimum film-forming temperatures, etc. (col. 7, lines 9-7).

In contrast, the polyurethanes of the present invention are thermoset, and as such, they do not possess any of the properties described by Kubota et al. and referred to in the previous paragraph. According to the Hawley reference: A thermoset polymer is a polymer "that solidifies or "sets" irreversibly when heated ... this property is usually associated with a cross-linking reaction of the molecular constituents ...." As evidenced by claim 1 of the present invention, self-crosslinkability of the polyurethanes is a property that is critical to the performance of the inks.

One requirement for establishing a *prima facie* case of obviousness is that the prior art references must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination must be found in the prior art, and not based on applicant's disclosure. Applicants submit that, by disclosing the use of thermoplastic polyurethanes in ink jet inks (and not polyurethanes in general), Kubota et al. do not teach or suggest to one of ordinary skill in the art that self-crosslinkable polymer particles that form a thermoset polymer could be used instead.

No motivation to combine reference teachings, no reasonable expectation of success

The Examiner states, in the Office Action of November 26, 2004, that Krepski et al. is "primarily concerned with pavement marking compositions," and that Krepski et al. "also teach that the disclosed coating composition is suitable for use on several types of substrate including paper." Applicants agree with these statements.

The Examiner also states that Krepski et al. disclose the use of the self-crosslinking particles "in coating for paper which is very similar to ink which is used to impart images, i.e., to coat, paper." Applicants respectfully submit that this is not so: paper coating compositions and

ink jet ink compositions are very differenct from each other. To say they are similar ignores *the methods by which each is applied* to the paper, and takes into account only the end result, i.e., the final product.

The Examiner also states that "it is significant to note that Krepski et al. disclose using silyl-terminated sulfopoly(esterurethane) in aqueous composition comprising pigment, dispersant, defoamer, wetting agent, etc. which is very similar, if not identical to ingredients found in ink compositions." To say that the ingredients are similar ignores the complexity of the technical issues that the experimenter must face when designing formulations for ink or paper coatings. The ingredients may be referred to as the same thing on paper, but small changes in the identities and the amounts of each of these ingredients may have huge effects on rheological properties of the formulations as well as their performance after being applied on a substrate. To illustrate the complexity, Applicant has assembled a collection of articles (copies are provided.) Selected excerpts are pointed out below.

An ink jet printhead is a sophisticated device that is designed to push an ink through micrometer-sized nozzles in a precisely controlled manner. Consider some of the requirements of ink jet inks as described in the article "Ink Technologies for Inkjet Printing" by P. MacFaul, *Surface Coatings International Part A: Coatings Journal,* 87 (10) , 420-426:

> "As the printhead technology has advanced in terms of faster printing speeds and smaller droplet sizes, the requirements placed on the ink have become more demanding." (page 1, 2nd paragraph)
>
> "The ink has to deliver a wide range of attributes that extend from printer storage, through jetting, to final image properties. Initially the ink has to be prepared with the correct viscosity and surface tension specifications for the printhead through which it is to be jetted. It must be non-corrosive to the materials which it comes into contact with, and it must not generate foam within the printhead as this will inhibity droplet formation. The ink must also be non-toxic as it could easily come into contact with the printer operators, and it must be stable with no chemical change, sedimentation or bacterial growth occurring for the shelf life of the print cartridge." (page 2, 1st paragraph)
>
> The droplets formed during the jetting process must have a constant size, shape and velocity, ... and must deliver good dot shape upon the substrate of interest. In addition, the inks must be able to withstand high jetting frequencies and have good re-start characteristics after the printhead has been left idle for a period of time. Finally, the image formed by the ink must be quick to dry, have the required shade and density, and

> deliver the required permanence properties such as light and waterfastness, highlighter smear and rub-fastness." (page 2, 2nd paragraph)
>
> "Ink manufacturers have been working for several years now to ensure that the inks can deliver all of the above attributes for various applications. *However, it must be stressed that the development of the ink is ideally made in conjunction with all the other critical parameters that go together to develop the complete printing system.*" (emphasis added; page 2, 3rd paragraph)
>
> "*However, <u>adding polymers to inks can result in serious jetting problems due to the increase in viscosity of these solutions</u>. As can be seen from the above discussion, the formulation development of aqueous inks is far from simple...*" (emphasis added, page 6, 1st and 2nd paragraphs).

Consider another article "Ink is integral part of printing process" by Jill Woods, *Converter,* September 2003, pages 26-27:

> "Today, a considerable amount of time and resource is invested in creating an ink that will optimize the performance of the new printing technologies, as well as provide the best possible end result..." (page 26, 2nd paragraph)
>
> "Digital technology, however, is setting a new trend, with processes such as digital inkjet having a much closer interdependency of the type of ink that is used. The nature of the printing process means that OEMs now work closely with ink specialists to develop inks that will provide optimal performance with printhead technology as well as the substrate and which are tailored to suit the end application." (page 26, 4th paragraph)

Consider yet another article "Inkjet Printing of Highly Loaded Particulate Suspensions" by Brian Derby and Nuno Reis, *MRS Bulletin,* November 2003, pages 815-818. In this article, a section entilted "Rheology of Particle Suspensions" (page 816) discusses the difficulties with printing particle-containing solutions. The take-away lesson from this article is that not all particles are created equal, i.e., they all have different effects on rheological properties, especially viscosity, and just because one type of particle might be suitable for use in an ink jet ink, does not mean that another would be.

In contrast to inkjet printing using an inkjet printhead, consider a review of coating processes that are used to coat paper in "A Review of Paper Coating" by T. Fukui, *Kami Pa Gikyoshi/Japan Tappi Journal,* 55 (12), 3-19. The abstract talks about five periods of coating methods and materials going back to 1910, and mentions that they are continuing to evolve to match market demands and obtain high productivity. Although the article is in Japanese, the 39

figures are in English, and they provide the reader with an overall feel for how complicated coating technology is. Most of the figures diagram different coating processes and equipment, and the rheology that the respective coating compositions must have is shown by graphical representations. Thus, one cannot readily assume that formulations useful in one coating process could be useful in another, yet alone be useful in an ink jet ink.

In the article "Three-Phase Approach to Coating Formulation Secures Startup Savings" by D. Spriggs, *Pulp & Paper,* 78(9), 63-65, the author gives an overview of what is involved in designing formulations for paper coatings. For example, the author describes on the last page, 2nd column, that for any single startup involving a coating process: screening and fundamental work can take anywhere from 3 to 6 months, pilot coater trials can take up to a year, optimizing rheology and operating conditions another 3 to 6 months, and end-user testing another 3-6 months. This article is worth reading from the beginning because it provides one not skilled in the art of coating paper a feel for what is involved at a hands-on level.

To establish a *prima facie* case of obviousness, at least two criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success.

Applicant submits that one of ordinary skill in the art of making ink jet inks would not be motivated to combine reference teachings of Kubota et al. and Krepski et al. One of ordinary skill in the art of ink jet inks would be motivated by Kubota et al. to find polymer materials that are thermoplastic so that they would have the appropriate softening temperatures, etc. One of ordinary skill would not be motivated to look to replacing thermoplastic polymer particles with self-crosslinking particles because the properties of the particles are critical for jetting performance. Even if one of ordinary skill in the art would be motivated to look to references related to paper coating compositions, one would not have a reasonable expectation that similar formulations or individual components would work, considering the complexities of the technologies. Applicants respectfully request withdrawal of this rejection.

Claim Rejections – 35 USC § 103 – Zhu et al. in view of Krepski et al.

Claims 1-5, 9-16, 23-25, 27, 31, 34-39, and 42-48 stand rejected under 35 USC § 103(a) as being unpatentable over Zhu (US 5,889,083) in view of Krepski et al. (US 5,929,160). The Examiner states that Zhu discloses an ink jet ink comprising 1-40 wt.% of polyurethane.

Zhu discloses that binder resins may be used in ink jet inks of their invention, and that an example is a polyurethane (col. 6, line 22-29). Applicants submit, however, that Zhu does not teach or suggest "the use of generic type of polymer, i.e., polyurethane" as stated by the Examiner. Instead, one skilled in the art would assume that Zhu is teaching the use of thermoplastic polyurethanes, as suggested by the following exerpts: "A binder resin should be film former which upon drying of the ink leaves a film on the colorant." (col. 4, lines 49-50); "The glass transition temperature of the binder resin is typically in the range of from about 50°C to about 100°C..." (col. 5, lines 8-11); and "The film, in combination with the wax and other ingredients of the ink composition, also provides the jet printed messages a measure of protection against abrasion." (col. 4, lines 53-54). The polymer described in the present claimed invention does not require drying to form a film (it merely has to crosslink), does not have a glass transition temperature (thermoset polymers do not have glass transition temperatures), and is not compatible with waxes (waxes would interfere with the crosslinking reactions).

As described above, in order to establish a *prima facie* case of obviousness, the prior art references must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination must be found in the prior art, and not based on applicant's disclosure. Applicants submit that, as described for the previous rejection, Zhu does not teach or suggest to one of ordinary skill in the art that self-crosslinkable polymer particles that form a thermoset polymer could be used. Applicants respectfully request withdrawal of this rejection.

Claim Rejections – 35 USC § 103 – Erdtmann et al. in view of Krepski et al.

Claims 1-2, 4-9, 15-16, 23-25, 27-30, 32-37, 40, 42, 44-49, and 51-52 stand rejected under 35 USC § 103(a) as being unpatentable over Erdtmann et al. (US 6,533,408 B1) in view of Krepski et al. (US 5,929,160). The Examiner states, in the Office Action of November 26, 2004,

that "Each reference discloses the use of generic type of polymer, i.e., polyurethane, with no disclosure of specific types of these polymers utilized."

Applicants respectfully disagree with this statement. Specific types of polyurethanes are disclosed in Erdtmann et al., and they are designated PU-1, PU-2, and PU-3 (col. 11, line 41 to col. 12, line 40). In addition, glass transition temperatures are reported in Table 1 (col. 13). Applicants submit that, for reasons sim Erdtmann et al. do not teach or suggest "the use of generic type of polymer, i.e., polyurethane" as stated by the Examiner. Instead, one skilled in the art would assume that Erdtmann et al. are teaching the use of thermoplastic polyurethanes because glass transition temperatures are reported. In addition, Erdmann et al. state that inks should exhibit "high pH stability characteristics" (col. 1, lines 56-57). In comparison, the self-crosslinking polymer particles of the present invention are not stable under high pH; a high pH would cause hydrolysis of the silyl groups which are critical for the crosslinking reaction.

As described above, the prior art references must teach or suggest all the claim limitations in order to establish a *prima facie* case of obviousness. The teaching or suggestion to make the claimed combination must be found in the prior art, and not based on applicant's disclosure. Applicants submit that, as described above, Erdtmann et al. do not teach or suggest to one of ordinary skill in the art that self-crosslinkable polymer particles that form a thermoset polymer could be used. Applicants respectfully request withdrawal of this rejection.

Applicant believes that the application is in condition for allowance; reconsideration is respectfully requested.

Respectfully submitted,

5-18-05
Date

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Methodical approach focused on raw material selection, testing, and formulation balance optimizes coatings for faster startups and salable paper production

Three-Phase Approach to Coating Formulation Secures Startup Savings

By **DON SPRIGGS**

Starting up new equipment after a rebuild or an installation may be one of the most rewarding and anxious moments in a production manager's job. A startup represents the culmination of months, even years, of hard work. And in the right market environment, the difference between a successful startup and a bad one can be as much as $250 million.

On the plus side, a startup offers the potential for higher efficiency and production rates to compete effectively in the global marketplace. Upgraded equipment not only enables paper mills to keep labor costs under control, it allows them to produce new paper grades and products, keeping pace with changes in the industry that can capture new customers. Installing new equipment, however, requires a tremendous capital investment up front, and a delayed or mishandled startup can be devastating from a cost standpoint.

Start the Startup Right

The cost for a new facility can easily reach $1 billion, and major rebuilds often cost in the range of $200 million to $500 million. With that kind of investment, paper companies and the people supplying the capital are understandably eager to begin making salable product as quickly as possible. And the greater the startup's tonnage potential, the more important planning becomes for achieving a commercial success (Figure 1).

Part of the delicacy of a paper machine startup stems from its complexity. Startups in this industry are far more elaborate than startups in other industries. For example, a modern paper machine has more than 5,000 control loops, whereas a modern airplane has only about 1,000.

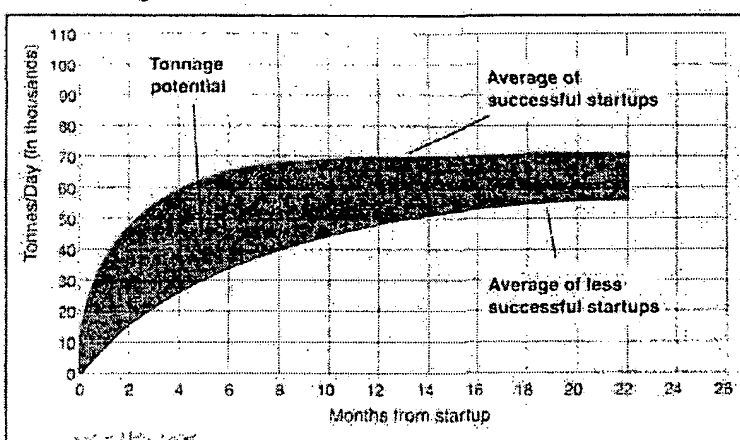
A paper machine startup necessitates integration of different science and technology elements, such as colloidal chemistry, mechanical engineering, market analysis, process control, physics (flow, drying, heat transfer, radiation), and sophisticated measurement systems (coat weight, moisture, hole detectors, web break detectors). Selecting the right coating formulation and appropriate application conditions is one part of this complex process. The chosen formulation must integrate with all these different pieces of the puzzle to achieve the best paper quality. Otherwise, the startup will never reach its full potential.

A successful startup means achieving the desired paper quality and new product sales as planned. The Dow Chemical Co. has participated in more than 70 successful machine startups globally during the past ten years. It has experience with selecting coating formulations for specific equipment, market knowledge, and a portfolio of high-performance binders that have helped customers achieve quality and sales goals during the startup process.

Based on this experience, three elements—raw material selection, testing, and formulation balance—have been shown to create an optimal coating formulation, as well as a successful startup, if executed carefully. Rapid ramp up capability in the first twenty-four months and 85% efficiency are not pipe dreams. However, since no startup can predict every troubleshooting scenario, customers need to plan fallback positions and find resources that offer immediate access to labs, industry experts, and equipment that can help resolve unforeseen problems. Such expertise can help, for example, when some presses have difficulty running a new product.

FIGURE 1.

Startups with a higher tonnage potential mean that planning is even more critical to achieving a commercial success.



Statistical Design for Materials Selection

The first step in developing a formulation is to identify and select the raw materials to reach the specifications of the identified market segment. The right pigment combination will achieve the optimum gloss, brightness, and opacity. The binder is just as important, because its ratio with the pigment will determine strength, ink coating interaction, stiffness, and converting properties. Additives help to optimize runnability, ▶

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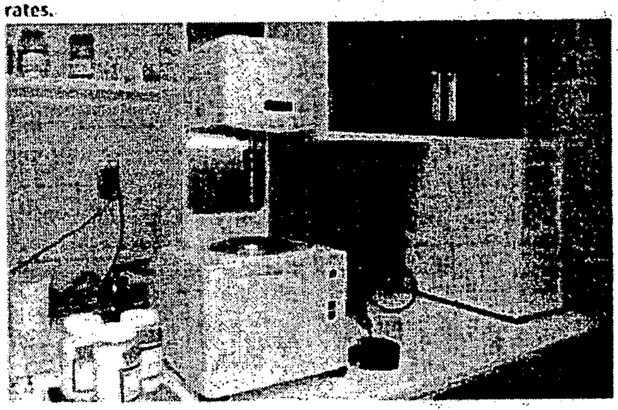
The use of capillary rheometers to obtain high shear viscosity data is recommended, since most coaters operate at very high shear rates.



optical properties, coating structure, and surface energy.

Selecting the startup raw materials and ensuing formulation is an effort to identify the best possible balance between end-use application properties, coater runnability, and cost. With a range of papers, from ultra-lightweight coated (LWC) base (less than 30 g/m²) to heavyweight recycle board (greater than 360 g/m²), at a variety of speeds and web paths, each application presents its own unique challenges.

A good tool to use when developing formulations is a statistical Design of Experiment (DOE). Normally, a trial-and-error search for a few critical factors that most affect coating performance is costly and time consuming. A DOE allows the team to efficiently and quickly screen numerous ingredients and levels of these ingredients in a manageable lab-scale study. From this screening study, suitable ingredient candidates can be determined and then more focused studies can be performed.

Beyond selecting the best raw materials, a startup formulation must be optimized for the selected application system. Factors such as rheology and immobilization characteristics need to be evaluated to ensure that the new coater is providing excellent runnability and high coater efficiencies.

Testing of Runnability and Performance

Once the raw material selection is narrowed down to the candidates with most potential, the next step is to test runnability and performance on the new equipment. Most often these tests are started in a laboratory environment to allow for a broad screening of formulations and their performance attributes.

The "runnability" of coatings can be predicted by a combination of rheology and immobilization rate measurements. Rheology needs to be measured over the whole shear rate range with rotational or capillary viscometers. Since most coaters operate at very high shear rates, more representative high shear viscosity data can be generated using a capillary rheometer. Depending on the applications system, additional factors such as visco-elasticity or extensional viscosity should be taken into account. Knowledge of the coating's immobilization properties is also critical, and this information can be generated by combining immobilization solids measurements with static and dynamic water retention testing.

Every coating application system requires a specific combination of rheology and immobilization characteristics. In addition, those properties need to be optimized over the desired speed range.

After the "runnability" tests are used to narrow the coating formulation candidates, the focus is then placed on further optimization of paper and print performance properties. In addition to the standard tests that are normally used to characterize coated paper, it is important to understand the paper and ink interactions.

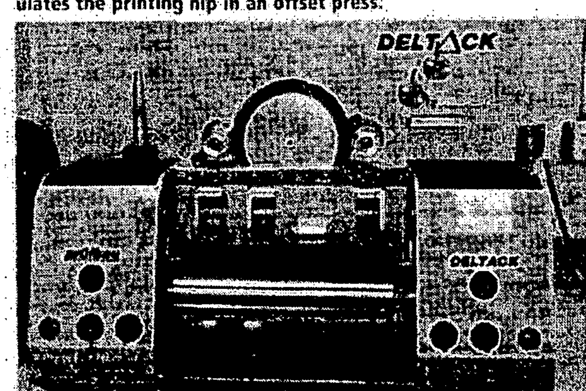
A very effective tool to measure how the ink and coating interact is the Prufbau Deltak, which is an instrument that simulates the printing nip in an offset press. The Deltak measures ink tack over short time periods and the onset of coating failure for paper and paperboard surfaces, using a standard quickset ink. This data is much more useful to the team than data from simple dry pick testing.

Coating strength is very dependent on the binder type and amount. More is not always better. Too much binder gives a strong coating, but can cause other problems such as fountain solution repellency, low sheet gloss, and poor blister resistance. The press performance can be predicted from paper lab tests of pilot coated paper, and ultimately will be confirmed during press trials that occur before, during, and after the startup.

While a lot of the testing can be accomplished on a laboratory scale, all identified formulation solutions need to be tested on the industry scale pilot coaters. This is to validate the coater runnability of the formulations and to allow full-scale print trials to evaluate end use performance.

At a later stage of the project, the pilot coater trials are often used to create commercial sample quantities to demonstrate

A very effective tool to measure how the ink and coating interact is the Prufbau Deltak, which is an instrument that simulates the printing nip in an offset press.



the coating formulation's performance on a larger scale. This can sometimes include working with test markets to gather valuable customer feedback on paper performance.

Formulation Balance: A Mixture of Challenges

Achieving the right balance in a formulation means finding the right mix between end use application properties, trouble-free applications, and cost. An important element in this part of a startup is employee training. Operators must familiarize themselves with the new equipment and how it works, as well as troubleshooting methods. They should make sure their understanding is solid enough that the paper quality will stay superior for the long-term use of the machine.

Equipment manufacturers and other experienced suppliers can help train mill employees on application technology. At the mill's expense, problems and complications can arise if employees don't know how to operate the machinery properly, fix minor problems, apply the right settings for a particular paper grade, or adjust those settings for optimum quality.

Proper coating make-down is also a critical aspect of making a quality product. A qualified coating supplier is able to provide advice on the preferred order of addition to avoid potential incompatibilities and poor mixing. It can also give guidance on good raw material acceptance procedures and testing to minimize the chance of mistakes when offloading the coating ingredients.

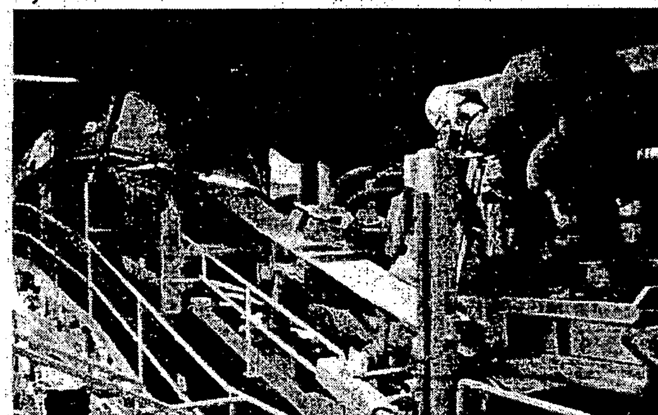
Even after employees have been trained, there may be a need to further optimize the formulation for troubleshooting needs. A mill has to make sure that every last detail is accurate: adjusting the formulation rheology, improving runnability, and optimizing the printability. It is critical to have options ready to address problems or changes in product specifications at the eleventh hour. Finally, a plan should be made for the new paper grade. Final standard specifications should be set, ensuring that the startup is producing a differentiated product that is competitive in the marketplace.

Coating Case History: Kruger Wayagamack

Daniel Tremblay, production manager at Kruger Wayagamack in Trois-Rivières, Que., has worked with Dow's coatings experts on a recent startup. The startup team spent several months of preparation working out the formulation and testing it. "We made a point of incorporating input from all suppliers, and we were able to develop a strong formulation that had almost no issues for our application," said Tremblay.

Work began in the laboratory on formulation development using lab tests designed to simulate printing conditions. Since Kruger Wayagamack required testing for specific application methods, as well as drying and finishing conditions, the testing then moved to its supplier's pilot coaters.

Pilot coaters are often used to create commercial sample quantities to demonstrate the coating formulation's performance on the larger industry scale.



Here, knowledge of the market played a crucial role in the final formulation testing. Several of Kruger Wayagamack's early trials were run in Europe using European formulations. Dow's experience in Europe, as well as their overall knowledge of the North American market needs, played a critical role in overseeing and analyzing these tests.

"Through all the trials, the process was smooth and looked simple, but that was because the preparation was good and the team had the right experience," Tremblay said.

The initial testing for general screening and fundamental work can take anywhere from three to six months, while the pilot coater trials used to validate the coating concept and determine the feasibility of the desired paper quality can take up to a year. Papermakers can count on another three to six months in order to optimize the rheology and operation conditions, and yet another three to six months to test the paper for multiple end-use properties. The final definition of the formulation and grade specifications on the pilot coater scale can add another additional six to twelve months to the lab trials.

All these tests might seem a bit extensive and time consuming, but it can mean the difference between a successful startup and a bad one, a difference that can translate into millions of lost dollars for a mill.

With a startup scenario like the one at Kruger Wayagamack, formulation balance means incorporating all these factors to create the most competitive product from a performance and trouble-free viewpoint.

"Most press rooms pass our paper with no problems," says Tremblay. "Now we're working with our supplier to determine how to make our product run on every press room with zero problems." **P&P**

RANIER KNAPPICH *is North American technical services and development leader for Dow Chemical, Midland, Mich.*

Inkjet Printing of Highly Loaded Particulate Suspensions

Brian Derby and Nuno Reis

Abstract

Inkjet printing is an attractive method for patterning and fabricating objects directly from design or image files without the need for masks, patterns, or dies. In order to achieve this with metals or ceramics, it is often necessary to print them as highly concentrated suspensions of powders in liquids. Such liquid suspensions must have physical properties appropriate to the inkjet delivery mechanism. These properties are presented using a nondimensional formalism to illustrate the requirements for both drop formation and spreading on impact. Further critical issues relevant to inkjet printing of particulate suspensions are discussed and illustrated with experiments on a model alumina-containing colloidal suspension.

Keywords: ceramic processing, fluid behavior, freeform fabrication, inkjet printing, particulate suspensions, rheology.

Introduction

Inkjet printing was originally developed in the 1970s as a contactless printing method. Inkjet printing is now a ubiquitous technology and is routinely used for personal printing, commercial printing, and product marking. In the broadest sense, inkjet printing is a method of generating droplets of precise volume and selectively depositing these droplets. This concept has led to a series of applications in the fields of microdosing and precision fluid dispensing, rapid prototyping, and rapid manufacturing. In this article, we will explore the use of inkjet printing as a method for the manufacture of small components with electrical and mechanical applications.

Inkjet printing deposits material in the form of a liquid. Therefore, in order to use inkjet printing to fabricate metal or ceramic parts, it is necessary to deliver the metal or ceramic materials in a liquid precursor form. The simplest way to achieve this is to disperse the required material as a fine powder suspended in a suitable liquid vehicle. The preparation and manipulation of powder-filled slurries is an important part of conventional powder processing technologies that have been applied to both ceramics and metals for many hundreds of years—for example, dissolving clay in water to form pottery slip, and depositing suspensions of oxides and metals as glazes and enamels. However, the required rheological properties of slurries usable for inkjet printing differ considerably from those used in many conventional forms of powder processing (e.g., screen printing or powder injection molding).

Inkjet printing has been explored for a number of years as a tool for ceramic fabrication. Initial work by Sachs et al.[1] did not directly print powder suspensions but instead printed a solution of binder materials onto a flat bed of metal or ceramic powder. This technique selectively bonds the powder patterned by the printed binder phase. A three-dimensional architecture is obtained by depositing subsequent powder layers followed by further printing. On completion of the process, all unbonded powder is removed and the resulting powder assembly is further consolidated by heat treatment. This method has been subsequently developed to allow for better densification rates and composition variation in the powder bed.[2] However, the process is limited by the requirement of depositing layers of powders. Direct inkjet printing of slurries is a more versatile method for the manufacture of ceramic and metallic parts and was pioneered by Evans and co-workers.[3–6] Less material is wasted, and by using multiple printing jets, it is possible to fabricate components of composite architecture or graded composition. Evans' initial work used alcohol and aqueous suspensions, but because this required an adapted printer normally used for graphics printing on paper, only fluids of relatively low viscosity could be printed, which limited the choice to relatively dilute suspensions containing <10% solids by volume.

There are two different mechanisms used to generate droplets in inkjet printers:

1. Continuous inkjet printers project a stream of liquid through a small orifice. The stream breaks up into small droplets by means of the Rayleigh instability, in which surface tension disrupts a liquid column into spherical particles; in commercial printers, the process is assisted by a mechanical oscillation near the orifice to ensure uniform droplet size and formation rate. An electric charge is imparted to the drops as they are formed, and these drops are steered to the desired substrate location by applying an electrostatic field. Drops not required for printing (e.g., when a space character is desired in text printing) are captured and recirculated.
2. Drop-on-demand (DOD) inkjet printers form individual drops of liquid by generating pressure waves in a liquid-filled cavity. For printing particle suspensions, this is normally achieved using a piezoelectric actuator. The pressure pulse ejects drops from an open orifice, which normally contains the liquid by surface tension. The drops are only formed when required, and spatial control is achieved by mechanically positioning the print head above the desired location before drop ejection.

Both methods of inkjet printing have been used successfully to build ceramic objects.[4,5] Continuous inkjet printing operates at much faster droplet generation rates than DOD printers; however, the need to use an electrically conducting fluid and the possibility of contamination during the recirculation process are limitations for many applications. Hence, piezoelectric DOD printing is preferred for the deposition of ceramic or metal suspensions.

Fluid Properties

The physical properties of the fluid in an inkjet printer strongly influence the drop formation mechanism and subsequent drop size and velocity for a given excitation (pressure) pulse. Early studies of drop-on-demand inkjet printing by Fromm[7] and Dijksman[8] identified the key physical processes of drop formation:

1. Generation of a pressure wave by mechanical vibration of the actuator and propagation of the wave through the fluid-filled chamber toward the orifice;
2. Deformation of the meniscus at the orifice and extrusion of liquid from the chamber; and
3. Instability of the extruded liquid column and subsequent drop formation.

The physical parameters of the fluid that are important in these three processes are the speed of sound (which determines the velocity of the pressure wave), viscosity, density, and surface tension. Although most of the earlier work modeled a simple, cylindrical, piezoelectric-actuated tube as the droplet generator, the fundamental physics of droplet formation is still the same in more modern designs.

In his analysis, Fromm used a dimensionless grouping of the fluid properties in order to solve the Navier–Stokes equations of fluid flow and thus to model the fluid dynamics of the jetting process. This is given as

$$\frac{(\gamma\rho a)^{1/2}}{\eta} = Z^{-1} = \frac{N_{Re}}{(N_{We})^{1/2}}, \tag{1}$$

where Z is the Ohnesorge number, which is more generally described as a ratio between the Reynolds number (N_{Re}) and the Weber number (N_{We}), respectively, with

$$N_{Re} = \frac{va\rho}{\eta} \tag{2a}$$

and

$$N_{We} = \frac{v^2 a\rho}{\gamma}, \tag{2b}$$

where v is velocity, a is a characteristic dimension (taken as the radius of the printing orifice), and ρ, η, and γ are the fluid density, viscosity, and surface tension, respectively. In most commercial DOD printing platforms, this dimensionless grouping has a value falling somewhere between 1 and 10. The influence of this dimensionless grouping on inkjet behavior has been explored using a fluid dynamics simulation.[9] If it is small, the viscosity is the dominant parameter and a large pressure pulse is required to eject a droplet. This leads to low droplet velocity and shorter fluid column extensions before droplet ejection. A high value of the numerical grouping leads to very large liquid column extensions before droplet formation. Such long columns usually lead to satellite drop formation behind the main drop.

Fluid properties are also very important during the process of droplet spreading on impact. A static drop on a solid surface will spread to its equilibrium shape and contact angle as determined by surface tension. However, the impact of a droplet from an inkjet printer, traveling at speeds of a few meters per second, is a dynamic process, with the droplet spreading initially to a greater contact area than the equilibrium value because of the contribution of kinetic energy. If inkjet printing is used to deposit components of controlled composition or if the spacing between printed tracks is important, the maximum spread of a drop on impact is a parameter equally as important as its equilibrium extent. The spreading process has been modeled by Pasandideh-Fard et al.,[10] who considered the balance between the kinetic energy of the deposited droplet and the increase in surface energy, along with viscous dissipation, as the droplet spreads. They found the following relationship for the ratio $\xi = d_{max}/d$, where d_{max} is the maximum diameter of spreading and d is the radius of the impinging droplet:

$$\xi = \frac{d_{max}}{d} = \left(\frac{N_{We} + 12}{3(1 - \cos\theta) + 4(N_{We}/N_{Re}^{1/2})}\right)^{1/2}, \tag{3}$$

where θ is the equilibrium contact angle of the droplet on the substrate.

It is possible that a rapidly spreading droplet will destabilize and splash on impact. A generally accepted parameter used to predict the onset of splashing on drop impact[11] is given as

$$K = N_{We}^{1/2} N_{Re}^{1/4}. \tag{4}$$

When K exceeds some critical value (K_c), which depends on substrate condition and temperature, splashing occurs.

Equations 1–4 can be used to determine the rheological properties of a fluid to make it suitable for inkjet printing. Figure 1 shows a N_{Re}–N_{We} parameter space onto which some of these relations have been mapped. The bold line across the top right corner shows where splashing occurs for $K_c = 100$, which is a typical value for the fluids used in our work. The two parallel dotted lines indicate the $1 < Z^{-1} < 10$ region in which inkjet printing is usually conducted. The three solid curves indicate various degrees of droplet spreading on impact. Superimposed upon this diagram are points indicating a range of fluids for the case of printing through jet orifices of 60 μm and 75 μm diameters under various driving conditions.

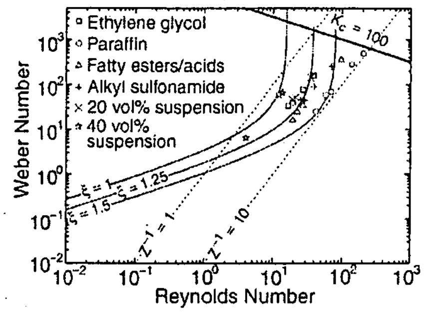


Figure 1. The influence of fluid properties on printing conditions in terms of Reynolds and Weber numbers. The solid curves indicate contours of equal maximum droplet spreading. The dotted lines indicate the boundaries of fluid properties typical of inkjet printers, and the bold line in the upper-right corner indicates the onset of splashing.

Rheology of Particle Suspensions

It is clear from the previous section that the physical and rheological properties of a fluid are very important in controlling its behavior during both droplet generation and impingement on a substrate. In order to print particulate suspensions, it is necessary to understand and control the rheological behavior to match the window of inkjet operability. It is not within the scope of this article to exhaustively discuss the methods used to produce stable suspensions of ceramic particles. Briefly, this is achieved by modifying the surface forces on the particles. In nonpolar media (i.e., low dielectric constant fluids), polymeric surfactants are often used; in polar solvents, a combination of polymer surfactants or modifications to the concentration of ions in solution is commonly employed.[12]

The fluid behavior of particle suspensions is a major subject in its own right. In order to print ceramics or metals, it is evident that the larger the volume fraction of particles in suspension, the more efficient the printing process in terms of deposition rate. It is well known that the viscosity of a suspension increases as the fraction of particles in suspension increases. For dilute suspensions (typically <2% by volume), Einstein's generalized equation states[13]

$$\eta = \eta_0(1 + A\phi), \tag{5}$$

where η is the viscosity of the suspension, η_0 is the viscosity of the fluid vehicle in the absence of particles, ϕ is the volume fraction of particles in suspension, and A is a constant that depends on the particle shape. However, in order to efficiently print metals and ceramics, the volume fraction of particles in suspension must be at values much larger than the dilute systems for which Equation 5 is valid. At a high content of solids, the increase in particle–particle interactions requires a more complex approach; empirical relations are used instead to describe the viscosity. One such relation in general use is a modified Krieger–Dougherty equation:[14]

$$\eta = \eta_0\left(1 - \frac{\phi}{\phi_{\max}}\right)^{-n}, \tag{6}$$

where $\phi_{\max}$ is the maximum volume fraction of solids in suspension, and n is an empirical constant. The maximum volume fraction occurs when there is sufficient direct particle–particle contact in the suspension for it to behave as an elastic solid and is typically in the range of 50–60% for equiaxed particles.

Equation 6 illustrates the dichotomy that occurs when developing particle suspensions for inkjet printing. It is desirable to maximize the solid loading of the suspension (i.e., maximize ϕ), but at the same time, the fluid viscosity must not exceed a value above which printing is not possible. Most commercial inkjet print-engine manufacturers specify a maximum fluid viscosity of about 20 mPa s. Figure 2 shows the viscosity of a polymeric stabilized colloidal alumina suspension in a hydrocarbon medium as a function of particle volume fraction. The trend in viscosity clearly follows Krieger–Dougherty behavior, with an exponent of approximately 2 and a maximum apparent volume fraction of about 53% (the actual, or effective, particle volume fraction is larger because it includes a contribution from an absorbed layer of polymer that prevents particle agglomeration). Clearly, the challenge is to develop suspensions with low viscosity at sufficiently high particle content to allow efficient printing.

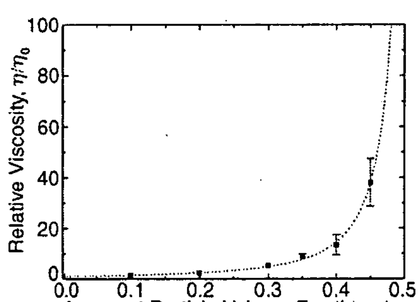


Figure 2. Viscosity of a colloidal alumina-filled paraffin medium as a function of solids loading (experimental points) fitted with a modified Krieger–Dougherty model: $\eta/\eta_0 = (1 - \phi/\phi_{max})^{-n}$, where η/η_0 is the relative fluid viscosity and ϕ is the apparent particle volume fraction in suspension; $\phi_{max} = 0.52 \pm 0.01$ and $n = 1.84 \pm 0.11$.

The viscosity of a suspension is normally non-Newtonian, that is, it is a function of strain rate. Inkjet printing generates droplets at very high shear rates. Considering the meniscus deformation that occurs to form a droplet, we can approximate the shear strain rate to that of the frequency of droplet ejection. DOD inkjet printers operate in the frequency range of 1–10 kHz; hence, the strain rates are expected to be in the range 10^3–10^4 s^{-1}. It is very difficult to make experimental measurements of fluid viscosity in this range of shear rates, and thus it is necessary to rely upon extrapolation from measurements made at much lower shear rates.

The pressures within a piezoelectrically driven inkjet droplet generator are very low—typically in the range of 100–500 kPa. Thus, fluid behavior should not show any yield phenomena, in that there should be no critical stress for minimum flow rate. Also, because we operate at strain rates much higher than those measured experimentally, the fluid should ideally show shear thinning behavior. Great care must be taken to ensure that no dilatancy (viscosity increasing rapidly with shear rate) occurs at high strain rates. Within an inkjet printer, dilatancy might occur within the constrained dimensions of the printer orifice if the particles interact with the walls and form an obstacle blocking the flow. In order to minimize this likelihood, the maximum size of the particles must be significantly smaller than the diameter of the orifice. From analogies with dry powder flow, the diameter of the largest particles present should be no greater than 1/20 of the orifice diameter.[15] Many commercial printer designs use an inline filter within the fluid supply system to ensure this.

Inkjet Printing Experiments

To illustrate the phenomena associated with inkjet printing of particle suspensions of either metals or ceramics, we will describe experiments carried out using a submicron alumina (Al_2O_3) powder suspended in a paraffin wax. Full details of the preparation of the ceramic suspensions used are given elsewhere.[16,17] Table I shows the fluid properties of the suspensions as a function of increasing volume fraction of particles. Although both suspension density and viscosity increase with increasing volume of particles in suspension, because of the exponential dependence of viscosity on volume fraction, the Reynolds number decreases rapidly until it is at the limit of printability (40% solids by loading).[16]

These materials were passed through a simple, single-orifice, piezoelectric inkjet droplet generator (Sanders Design International, Wilton, N.H.). Droplet properties (volume and velocity) were characterized as a function of operating parameters (excitation pulse voltage, frequency, and duration). Both droplet velocity and droplet size can be controlled, within limits, by altering the excitation signal to the piezoelectric transducer in the droplet generator.[17,18] However, droplet properties are strongly influenced by fluid properties. Figure 3 shows the influence of excitation frequency on drop radius for paraffin wax and the wax filled with alumina. There is a clearly visible periodic dependence on excitation frequency. This illustrates the acoustic characteristics of the droplet generator with

Table I: Fluid Properties of Alumina-Filled Paraffin Suspensions.[18]

ϕ	ρ (kg m^{-3})	c (m s^{-1})	η (Pa s)	γ (J m^{-2})	N_{Re}	N_{We}	Z^{-1}	K	ξ
0	770	1153	0.003	0.025	57.8	20.8	12.7	12.6	1.7
0.1	1093	1015	0.0045	…	54.7	29.5	10.1	14.8	1.6
0.2	1416	919	0.008	…	39.8	38.2	6.4	15.5	1.4
0.3	1793	876	0.015	…	26.9	48.4	3.9	15.8	1.3
0.4	2062	878	0.038	…	12.2	55.7	1.6	13.9	1.0

Notes: Average particle size, 0.3 μm; assumed droplet velocity, 3 m s^{-1}; characteristic length equal to the orifice diameter (75 μm).
ϕ = volume fraction of particles in suspension; ρ = fluid density; c = the acoustic wave speed; η = fluid viscosity measured at a steady-state shear rate of 80 s^{-1}; γ = fluid surface tension; N_{Re} = Reynolds number; N_{We} = Weber number; Z = Ohnesorge number; K = parameter used to predict the onset of splashing on drop impact; ξ = ratio of maximum diameter of spreading to radius of the impinging droplet.

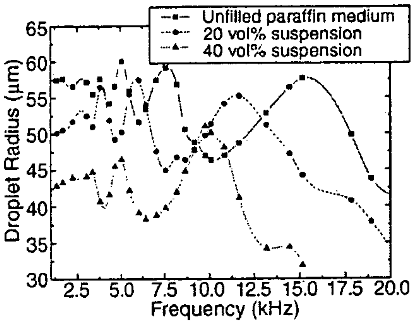


Figure 3. Ejected droplet size as a function of excitation frequency for a paraffin wax and paraffin containing different amounts of alumina powder in suspension. All inkjet driving parameters are held constant (pulse duration and amplitude of 32 μs and 60 V, respectively, at a temperature of 110°C).

clear resonance frequencies. The acoustic properties of fluid-filled cavities depend on the velocity of sound in the fluid; this is controlled by density and bulk modulus, both of which are functions of particle content. Thus, significant changes in drop size (and also drop velocity) are expected when there is a change in fluid, if all operating parameters are kept constant. Table I shows how the speed of sound and the Reynolds and Weber numbers change as a fluid is filled with an increasing amount of particles.

In order to print objects of controlled dimension using powder-filled liquids, it is necessary to control the deposited lines by controlling droplet size and velocity. At present, this is achieved by careful experimental characterization of droplet properties as a function of operating parameters for each suspension. These data can then be used to adjust the operating parameters of inkjet printers, by means of the software driver, to achieve the desired printing behavior. Thus, it is possible to print well-defined lines of ceramics and with these to build up three-dimensional objects that can then be sintered to full density.[17,18] An example of a sintered object produced by inkjet printing is shown in Figure 4.

To conclude, it has been demonstrated that it is possible to develop ceramic suspensions containing in excess of 40% solids by volume that can be passed successfully through inkjet printers. The limiting factor for printing objects is the conflicting requirements of a low fluid viscosity with a large fraction of solids in suspension. Printable ceramic suspensions of ZrO_2 and PZT have also been developed,[19,20] and in principle, given suitable surfactants, stable printable suspensions of any material available in powder form can be developed. Although the results presented here concern ceramic suspensions, the same principles are applicable to particulate suspensions of any material type.

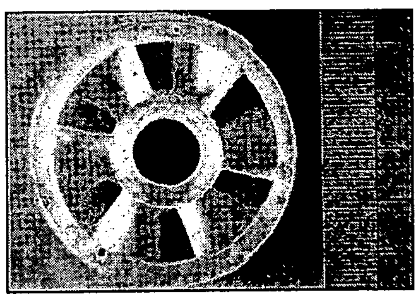


Figure 4. Example of a ceramic object produced by inkjet printing: sintered alumina impeller manufactured by three-dimensional inkjet deposition of highly filled suspensions directly from a computer-aided design file. The scale minor division is 1 mm.

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Ink is integral part of printing process

Jill Woods, inks and media product manager at Xaar, takes a closer look at the range of inks now available and in development for the digital inkjet market.

OVER THE past decade, the printing industry has undergone considerable change, most notably with the introduction of new digital printing technologies and sophisticated techniques to suit a range of different printing applications. But, as the printing process becomes more sophisticated, it is easy to forget that the ink market too has had to evolve and adapt to these new automated printing methods.

In many instances, ink is no longer seen as a single commodity, but with the development of new digital technologies, it has become an integral part of the printing process. Today, a considerable amount of time and resource is invested in creating an ink that will optimise the performance of the new printing technologies as well as provide the best possible end result, whether it is for printing brochures, large outdoor posters, simple barcoding or sophisticated brand packaging.

The recent past has been a turbulent time for the inks market, with the pressures of falling prices and environmental issues placing heavy burdens on manufacturers. Traditionally, printing methods such as screen, litho, flexo and gravure have not been dependent on the use of a particular ink to run through their presses, hence, in the past buying decisions were highly influenced by price and not always by quality.

Digital technology however, is setting a new trend, with processes such as digital inkjet having a much closer interdependency on the type of ink that is used. The nature of the printing process means that OEMs now work closely with ink specialists to develop inks that will provide optimal performance with the printhead technology as well as the substrate and which are tailored to suit the end application.

With this acceleration in the development of ink, there is now a wide range of inks to suit just about every machine and tailored to give the best results for any application. There are four main categories of ink that have found wide-ranging use in the digital inkjet market; aqueous, oil-based, solvent and UV cure inks.

The value of such inks may be linked to their flexibility to perform on an increasingly wide range of substrates and in high performance printing machines. It is important to note that inks are tough and are vigorously tested to meet the demand of intensified printing applications. Each ink type does vary and has its own set of independent properties - this is what sets inks aside from just being an additional printing tool and indeed from one another.

Oil-based inks for example are pigmented systems based on essentially non-drying, low volatility oils. They are only suitable for a limited range of substrates, namely paper and board, making them ideally suited to the packaging sector. The inks 'dry' rapidly on porous materials by absorption, but due to the nature of the oils, never dry on non-porous or semi-porous substrates. Oil-based inks are therefore the mainstay of industrial applications such as outer case coding and marking and have an excellent open time in printheads resulting in minimal maintenance requirements. For example, incorporating Xaar printheads, Alpha Dot's range of Merlin printers utilises oil-based inks to produce exceptionally clear and precise colour and black and white print quality onto a variety of substrates, from wood to plasterboard.

One thing to note however, is that the lack of glossy substrates capable of rapidly absorbing oil has resulted in limited use in wide format graphics applications (posters and banners), although impressive results can be achieved using cheap absorbent paper for traditional billboard applications.

In contrast, solvent-based inks are widely used in graphics printing applications due to their low cost and ability to print directly onto uncoated substrates such as banner vinyl, self adhesive vinyl, mesh and paper. The use of high quality pigments can provide good outdoor UV stability without the use of over laminates, whilst the volatile nature of the inks gives a low dried ink film weight.

Digital Graphics Incorporation's (DGI) utilises solvent-based inks with its Vistajet digital inkjet printer to achieve high quality images for the production of large banners that are specifically designed for outdoor use.

These inks are carefully formulated to provide a balance between the dry time characteristics on substrates and the open time in the printhead. Regular maintenance may be required, with capping of the printheads for example when the printer is not in use. In addition, when using non-porous substrates, it may require heating in order to produce rapid dry times and prevent ink mottling in high ink density areas. This said, solvent-based inks do provide high quality images and still remain a popular ink choice for a wide range of digital printing machines.

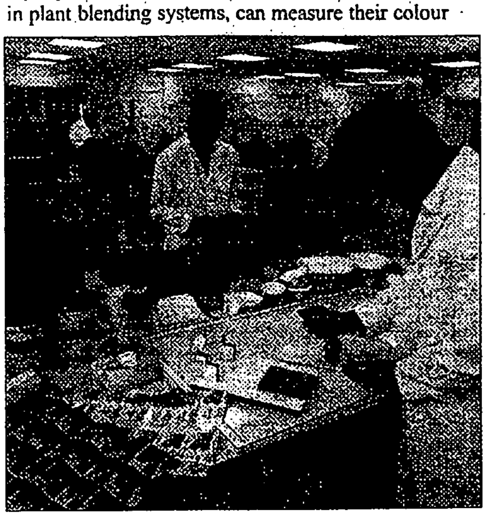
Solvent inks, however, don't come without a number of environmental implications. Due to their nature, they have a high level of volatile organic components (VOCs), which have a negative impact on the environment. Therefore the use, storage and disposal of solvent-based inks need to be controlled and they must be used in a well-ventilated facility.

An increasingly popular alternative to the solvent-based inks are UV curable inks, which are rapidly becoming the mainstay ink for the new generation of flatbed digital printers designed to print on a wide range of flexible and rigid substrates. Bright, tough and durable results can be achieved on uncoated substrates, therefore eliminating the need for over lamination for outdoor applications. The combination of UV inks and digital flatbed machines allow you to create outdoor media such as hoardings, billboards and banners reliably, productively and ultimately more quickly, hence this combined technology has excited the industry with its printing techniques creating a huge impact and increased promotional use.

Inca for example, has chosen to opt for a UV ink system for its Inca Eagle 44 flatbed printing machine. The machine has been designed to accommodate applications such as point of sale material and signage. With UV inkjet formulations being mainly acrylate-based 100 percent solids

Matching by remote control

REMOTE COLOUR matching has enabled Intercolor to respond to customers' needs more rapidly and accurately. Customers with Intercolor's in plant blending systems, can measure their colour sample with an sophisticated spectrophotometer and transmit the data over the Internet.



Once the colour laboratory has completed the matching, its data is fed back to the dispensing equipment in the customer's premises. An important element is the new colour correlated colour monitors at both ends.

However, the remote colour matching approach could not work without exceptionally consistent ink colour bases.

The highly pigmented bases are quality controlled to a tighter specification than is normally encountered in the industry. The result is that customers can have special colours on the press without delay and with confidence.

The key to its approach to the narrow web market is that they strongly encourage its customers to enter into a working partnership with them.

Jointly they determine the customers needs, both for the product and the supporting services, and develop both to match the requirement. **Enquiry 29**

formulations, the Eagle is able to print on to a wide range of substrates including board, wood, and plastics such as PVC.

Also utilising Xaar's piezo drop on demand inkjet technology with UV cure inks, the Canpet Printomat 400, is the first digital inkjet printer of cylindrical objects, allowing direct printing onto items such as beverage cans. Its short run, variable printing capabilities allow greater customisation and personalisation and appeal to packagers wanting to stand out from their competition by printing directly onto their products.

UV cure inks in addition are VOC free and remain liquid until cured (solidified) by exposure to UV light. This gives long open times and low maintenance requirements in the printhead, and almost simultaneous 'drying' on the substrate when exposed to UV light. However, UV cure inks can suffer from oxygen inhibition at the surface, which can lead to a tacky finish. The relatively high film weight can lead to poor through cure, which can in turn give adhesion failure. Both of these situations can be minimised or eliminated by careful formulation and the use of light sources with the correct spectral and power output characteristics.

Whilst UV cure inks are exempt from VOC emission regulations, they do require extraction for removal of ozone produced by the curing process. The nature of the monomers used to give the low viscosity inks required for inkjet printing means that UV cure inks need to be handled carefully as many formulations have a risk of causing a skin sensitisation reaction.

One of the latest developments in the industrial inks market has been the development of aqueous inks, which are low in cost and classed as environmentally 'friendly' and have tended to dominate the desktop printing market, in both dye-based and pigmented formulations. These inks are suitable for printing onto porous substrates but do require the use of expensive specialised substrates for optimum results and for outdoor durability, over lamination is required. Due to the nature of water, aqueous inks have a relatively long dry time on substrates, but have a tendency to dry rapidly in printhead nozzles, giving rise to frequent maintenance requirements. Capping of the printhead is also required when the printers are not ink use.

Looking ahead, I believe future developments in ink will include cationic systems which may well open the route to food packaging applications and water-based UV-curing systems which will provide a lower film weight and higher proportion of higher molecular weight, lower irritancy oligomers giving improved health and safety profiles.

Such inks would also be more suitable for use on porous / semi porous substrates, giving better cure performance and reduced odour.

Enquiry 30 ■

News in Brief

Pump up the volume

Powerwise has introduced the filter surge suppressor to counteract the pulsation problems associated with diaphragm pumps.

This effectively takes the surging away and makes the operators life easier. Cleaning is achieved by flushing through the pump with solvent or cleaning agent and water.

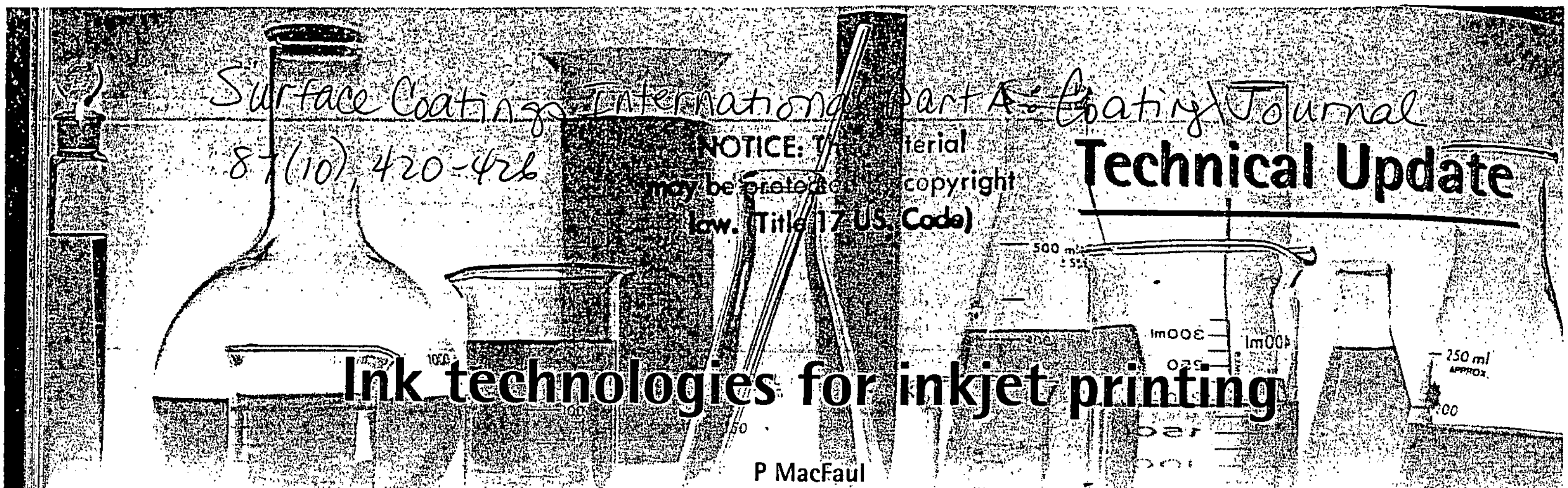
Powerwise has designed its centrifugal pumps to be user friendly and as simple to clean as possible. This style of pump is the standard bearer and, together with diaphragm pumps, form the mainstay of pumping systems used in the printing industry.

The three rod designed Trifugal nylon coated pumps are constructed from virtually all stainless steel components and hardware. This makes them excellent for use with water-based inks.

A by-pass is a must for mixing the ink uniformly within the container and is used as a flushing system for cleaning the press and the pump between press runs.

Powerwise says it has been supplying the industry for years and carries an extensive range of spare parts.

Enquiry 100 ■



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Ink technologies for inkjet printing

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Introduction

Although inkjet printing was developed during the 1960s and 1970s,[1-3] it was in the mid-1980s – when Canon[4] and Hewlett-Packard[5] successfully introduced printers for the home and small office markets – that the real growth in the use of inkjet technology was observed. Initially, the demands placed on the ink were associated with getting the colourants, mainly water-soluble textile dyes, onto paper using this new technology. This was primarily achieved by advances in dye purity and processing.[7,8]

As the printhead technology has advanced in terms of faster printing speeds and smaller droplet sizes, the requirements placed on ink have become more demanding. These developments in technology have also meant that new market areas have become available, placing further demands on the ink and, in some cases, requiring totally new approaches to ink development.[9] The use of inkjet technology can provide benefits on any occasion when the printing of variable information is required, and can save time and money when only short print runs are required.

This paper describes some of the features of the different types of ink that are available for a variety of digital imaging applications. Both aqueous and non-aqueous inks are discussed, together with the applications for which they are designed. In addition, the attributes that ink needs to display for inkjet applications are discussed, with an emphasis being placed on water-based ink, and the challenges that colourant developers and formulation chemists face in order to design superior aqueous inkjet inks.

Ink technologies

A variety of different ink technologies have been developed over the last few years for inkjet applications. These range from aqueous inks, which are found in most small office and home-based inkjet printers, to oil and ultraviolet (UV) cure-based inks which are more widely used in industrial and packaging-type applications. More novel applications that have begun to exploit inkjet technology, such as inks to prepare displays and printed circuit boards, have required the development of totally new ink chemistries.

Aqueous ink technology

Water-based ink represents the original and most flexible of the inks for inkjet applications. Aqueous inks have been developed over the last 20 years for both thermal and piezo inkjet printing systems. The main advantages over solvent-based inks are that they contain little or no volatile organic components. The initial application for these inks was in the small office or home markets, where it was desirable to be able to print text with some colour capability. The inks were originally based on water-soluble textile dyes, however, the inks that were prepared proved to be extremely unreliable with many nozzles becoming blocked. The dyes were then subjected to further processing and purification and, as a result, they could be jetted reliably using inkjet technology.

As the technology has expanded, the requirements placed on ink have also grown. For example, the output from inkjet printers for offices is now required to match laser printing text quality, or silver halide permanence for digital photography. To cope with these greater demands, dyes and pigment dispersions have been specifically designed for inkjet applications, where precise requirements are placed on both the ink properties of the colourants, and on the image properties. As the speed and flexibility of inkjet printhead technologies have increased, the number of different potential applications has also increased. Inks are now being developed for wide or grand format posters, textiles, colour proofing, photo mini-labs such as those found in supermarkets, commercial print jobs such as forms, statements, lottery tickets, addresses, as well as newspapers and security applications. There are now over 5000 patents relating to aqueous inkjet inks, with these being divided mainly into colourant and formulation patents. The design of, and the challenges facing, aqueous inks will be discussed in more detail later.

Non-aqueous ink technologies

100% solids UV cure

These pigmented inks contain a blend of monomeric and oligomeric acrylates that are polymerised using UV light in the presence of a photoinitiator.[10] As the inks contain no volatile organic compounds, the nozzles can be left uncapped for long periods of time, and as the rate of curing is fast, good line speeds can be achieved for production printing. The viscosity of the inks at the operating temperature is typically around 10cP, and the surface tension is in the region of 23 to 29 dynes/cm. To achieve good operability in the inkjet print heads the particle size of the pigments is below one micrometre. The printed film is instantly hardened on the substrate as all the ink components are chemically cross-linked on exposure to the irradiation. The inks give excellent print performance across a range of non-porous substrates (eg metals and plastics) and can be used for printing applications such as beverage can labelling and credit cards. The images that are formed have very high durability, with good resistance to chemicals and to physical abrasion.

Oil-based pigment inks

In this technology, the pigments are dispersed in a low viscosity, non-volatile oil.[11] Again the particle size of the pigments is less than a micrometre to ensure good operation, while to maintain good colloidal stability, polymeric hyperdispersants may be employed. The inks typically have a viscosity in the region of 10cP, with a surface tension below 30 dynes/cm, and tend to give excellent operability and long nozzle open times due to the lack of volatile components.

The use of these inks is largely for printing onto plain and coated papers, as well as coated vinyls, as the substrate needs to be able to absorb the ink. The images that are formed have excellent light and waterfastness, and as the inks contain no water there are no issues with cockling when printing onto paper substrates. In addition to barcoding, which is a major application for oil-based inks, these inks are used in various wide and large format applications, as well as in commercial printing (eg receipts and lottery tickets). They can also be used for addressing and franking within the mailing industry.

Printed circuit board inks

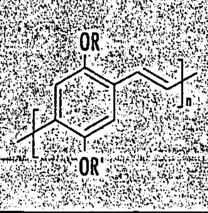
Inkjet technology has recently begun to be exploited for the manufacture of printed circuit boards (PCBs)[12,13] where great savings can be made in cost and time through a much simplified manufacturing process. The current method of producing PCBs involves numerous steps, many of which are costly and involve expensive hardware.

One example of such a simplified process is where curable circuit tracks are inkjet printed onto a copper coated substrate, the tracks are cured, the non-patterned copper is then etched away, and then finally the cured resin is removed to reveal the copper track. Another example is where the conducting tracks are directly deposited onto the substrates via inkjet printing of metal-containing inks. The use of inkjet can lead to significant reductions in the amount of waste generated, and is ideally suited to short runs where the designs can be rapidly amended.

Displays

The jetting of inks containing light-emitting polymers (LEPs) is being investigated as a way to produce cheap, energy-efficient displays.[14,15] LEPs such as poly (p-phenylene vinylenes) (see Figure 1) can be developed to emit red, green or blue light, and if dissolved in organic solvents under the correct conditions, they can be deposited using inkjet technology on specially developed substrates to produce low cost displays that consume much less energy than conventional liquid crystal displays. The key to success in this application is the accuracy of the droplet placement which inkjet is able to offer.

Figure 1: Poly (p-phenylene vinylenes)



Other ink technologies

A number of other ink technologies have been developed for various applications. Disperse dye and reactive dye-based inks, as well as pigment-based inks, have been developed for textile applications, where the inks are either jetted directly onto the fabric or onto transfer sheets to generate images.[16,17] These inks are only cost-effective for very short-run applications, for example design proofing or novelty printing.

Inks have been designed for various security applications, where the colourant is replaced with an active material such as an infrared absorber,[18] so that the printed image can then only be seen under certain lighting conditions. Applications for these inks include banknotes and counterfeit prevention.

In addition to 100% UV-cure inks, it is also possible to design aqueous based UV-curable inks that can be used on porous materials but still give highly durable images.[19]

Inks that undergo phase changes have also been developed; in particular numerous ink manufacturers have developed hot melt inks[20] where the ink is a solid at room temperature but liquid at the jetting temperature. Two-phase inks have also been developed where improvements in image properties have been delivered through the use of inks containing micro-emulsions.[21]

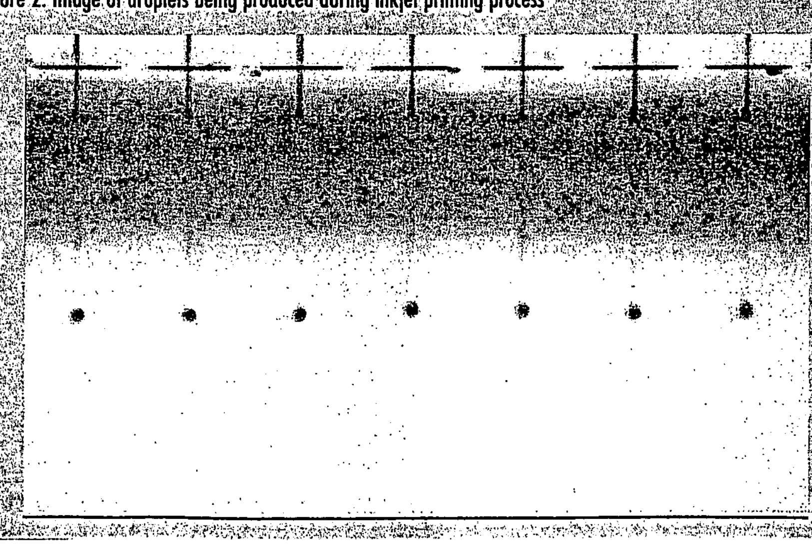
Ink attributes

The ink has to deliver a wide range of different attributes that extend from in-printer storage, through jetting, to final image properties. Initially the ink has to be prepared with the correct viscosity and surface tension specifications for the printhead through which it is to be jetted. It must be non-corrosive to the materials which it comes into contact with, and it must not generate foam within the printhead as this will inhibit droplet formation. The ink must also be non-toxic as it could easily come into contact with the printer operators, and it must be stable with no chemical change, sedimentation or bacterial growth occurring for the shelf life of the print cartridge.

The droplets formed during the jetting process must have a constant size, shape and velocity (see Figure 2), and must deliver good dot shape upon the substrate of interest. In addition, the inks must be able to withstand high jetting frequencies and have good re-start characteristics after the printhead has been left idle for a period of time. Finally, the image formed by the ink must be quick to dry, have the required colour shade and density, and deliver the required permanence properties such as light and waterfastness, highlighter smear and rub-fastness.

Ink manufacturers have been working for several years now to ensure that the inks can deliver all of the above attributes for various applications. However, it must be

Figure 2: Image of droplets being produced during inkjet printing process



stressed that the development of the ink is ideally made in conjunction with all the other critical parameters that go together to develop the complete printing system. The performance of the ink is dependent upon the manufacture of the printhead, as any imperfections in the manufacturing process will lead to deficiencies in the performance of the ink. In addition, the software that drives the droplet-generating process and writing of the images, together with the design of the substrate, can have a significant impact on the final image properties, including colour and image permanence.

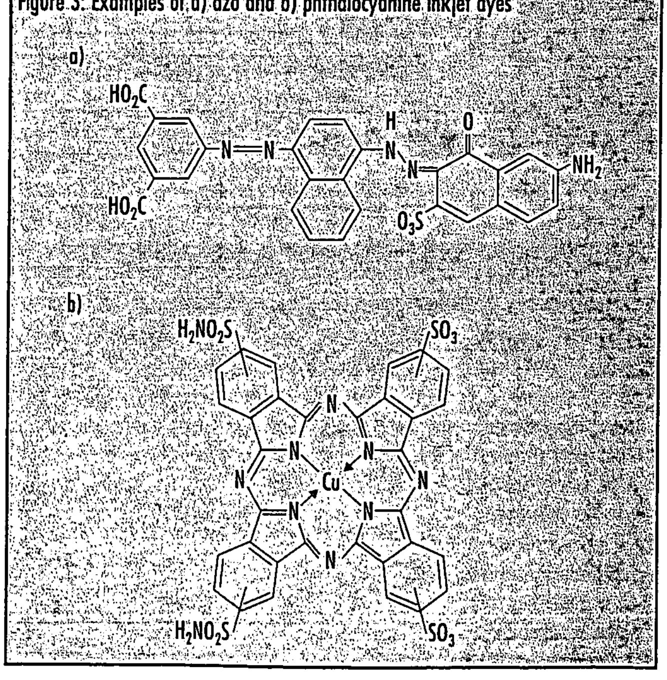
Aqueous inks: Formulation design and challenges

A typical aqueous ink is made up of several components, with the key component being the colourant. Additional constituents are selected to deliver the physical properties of the ink that are required in order for it to be jetted from the particular printhead for which the ink is being designed, to maintain good operability of that ink, to ensure that the ink is stable, and enhance the properties of the image generated from the ink.

In general, the ink will contain 2 to 6% colourant, 5 to 10% of a humectant (to prevent the ink drying in the nozzles) and 5 to 10% of a cosolvent (to enhance solubility of the dye), 0.1 to 2% surfactant (to adjust the surface tension), 0.1% buffer and 0.1 to 0.3% biocide. The ink may also contain other additives to adjust viscosity, penetration of the ink into the substrate, and compounds such as metal chelating agents, UV absorbers and antioxidants.

The colourant can either be a water-soluble dye, a solvent-soluble dye, or a pigment dispersion, the choice of which is determined by the particular application for which the ink is being designed. The dyes are usually based on azo or phthalocyanine chemistry (see Figure 3)[22] and incorporate sulphonic or carboxylic acid groups to achieve water solubility. The salt form of the dyes varies depending on the dye structure and the solubility of the complex, but is typically sodium, lithium or ammonium.

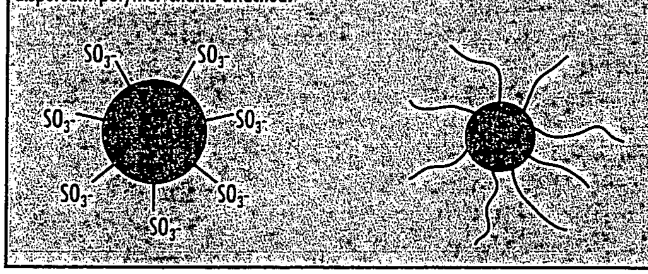
Figure 3: Examples of a) azo and b) phthalocyanine inkjet dyes



The main advantage of dyes include the large number of chromophores available that can be fine-tuned to deliver the specific colour needs of particular applications, together with the colour gamut and the formulation latitude that these chromophores can supply. In addition, dyes have very good special media (photographic) performance. However, it takes a special knowledge of these inkjet systems to develop dyes that give good permanence on microporous media, and in addition generally available dyes do not display good light or ozone fastness. Finally, as they are water-soluble, the dyes tend not to have good water fastness on plain papers.

To ensure that the pigment particles, whose typical particle size is in the region of 100 to 200nm, do not flocculate and cause nozzle blockages, either a dispersant is included in the ink[23] or the pigment particles are chemically modified so that they are self-dispersing[24] (see Figure 4). The main advantages of pigment-based inks are related to the colour density that can be generated, particularly for black images (text), and the permanence of images, where good waterfastness and excellent resistance to fading by light and ozone are observed.

Figure 4: Pigment dispersion technologies: a) chemically modified and b) with dispersant polymer chains attached.



However, pigments are, by their nature, particles, and it is not always straightforward to achieve the correct particle-size distribution or acceptable stability of the dispersion. In fact, if the colloidal dispersion is made too stable, re-peptisation of the pigments (re-dispersion of the coagulated colloidal particles in the presence of water) may occur, leading to less waterfast images. In addition, the images formed from pigments do not, in general, display the colour gamut available with dye-based inks, and as the particles are deposited on the surface of the substrate, they can be easily smudged or smeared. The performance of many pigmented inks is also unacceptable on glossy photographic media, as the particles tend not to penetrate the media surface, leading to unevenness of the surface resulting in poor gloss.

As mentioned earlier, once the colourant has been chosen, the remaining components of the ink are selected to deliver the required physical properties in order for the ink to be jetted from the particular printhead for which the ink is being designed. The two most critical physical properties of the ink that must be controlled are viscosity and surface tension. For current aqueous inks, the viscosity is typically in the region of 2 to 20cP, and the surface tension is between 25 and 60 dynes per cm. These two parameters control the wetting of the print head (priming), the flow of the ink through the print head, the position of the meniscus within the nozzle and the droplet generation.

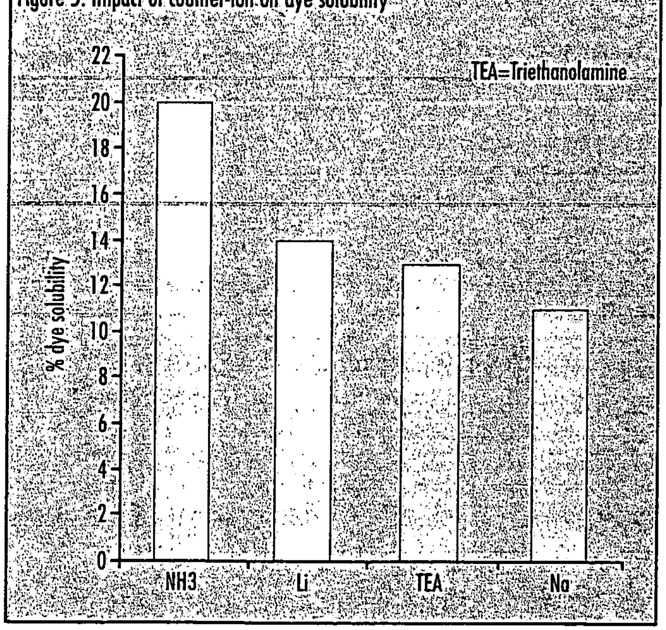
It must be noted that these parameters are specific for each particular printhead, and are determined by factors such as materials of construction, shape of the nozzles and ink chambers,

and the mode of droplet generation. The viscosity is usually controlled by the choice of solvents and, if necessary, by the addition of a polymer. The surface tension is controlled by the addition of surfactants and, to some extent, by the choice of solvents. All other changes made to the ink to deliver the required image properties must not result in these parameters being outside the range required to allow ink droplets to form from a particular printhead.

Once the ink has been designed such that it is found to jet well from the printhead, the formulation must be adapted to ensure that once printing is stopped, there are no issues with droplet formation when it is required to start again (re-start). The most common reason for failures on re-start is blockage of the nozzles resulting from evaporation of some of the water, which has induced precipitation or flocculation of the colourant. Two potential ways to overcome this problem are to add a humectant that inhibits the loss of water, and to add a cosolvent to the ink so that solubility of the dye or stability of the pigment dispersion is maintained even if some water is lost. These additives are typically compounds such as glycerol, ethylene glycol and pyrrolidones.

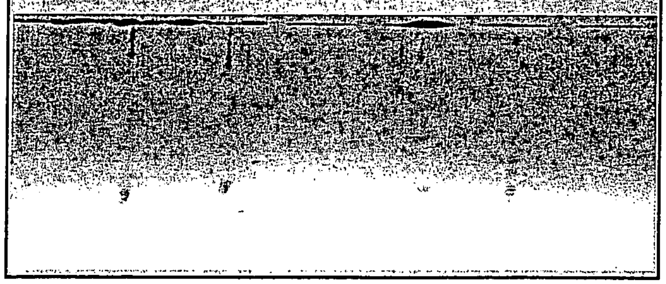
Another way to improve the re-start characteristics of the ink is to enhance the solubility or stability of the colourant through modification of either the dye structure or the pigment dispersion. In the case of dyes, the solubility can be increased through the addition of extra anionic groups or by changing the counter-ion; see Figure 5, for example, where the solubility of a dye is seen to dramatically vary as a function of the counter-ion.

Figure 5: Impact of counter-ion on dye solubility



On those print systems in which ink is jetted continuously and controlled by being directed towards or away from the target substrate (continuous inkjet), problems can be encountered due to ink pooling on the nozzle plate or by air being ingested into the firing chamber. Once this happens, droplets can be misdirected or nozzles can fail to fire altogether. Figure 6 illustrates the changes in the jetting characteristics that can be observed for an ink that has been incorrectly formulated. Compared with Figure 2, where all the nozzles can be seen to be firing well with all the droplets being ejected at the same speed and in the same direction, it can be seen that several droplets are being fired at different angles to the original jet, and that some nozzles are now no longer functioning at all.

Figure 6: Jetting instability observed with incorrectly formulated ink



These issues can usually be resolved by adjustment of the surface tension or viscosity of the ink, the pressure of the ink within the nozzles, and by purging the ink through the print head and wiping the nozzle plate. Obviously this latter solution results in down time for the printer and so, if possible, these issues are dealt with by correct formulation development.

Once the droplets have landed on the surface, the fluid begins to spread along and penetrate the media surface as well as starting to evaporate. The surface tension and viscosity of the ink play an important role in determining the ratio of these first two effects, and therefore impacts directly on print characteristics such as dry time, feathering, strike-through and optical density (OD). The location of the colourant within the media can also be affected by the ink properties, and therefore the durability of the image in terms of rub and waterfastness, and also resistance to fading by light and ozone, can be impacted by the ink design.

In addition to all the jetting and image criteria, an ink must have an acceptable shelf life. Inks are generally tested under accelerated conditions, for example, they are stored for several weeks at elevated temperatures or under freezing conditions, in addition to being subjected to temperature cycling studies. Any changes in the chemical or physical properties of the ink need to be minimised, and several different types of additives (summarised in Table 1) are incorporated in the ink to aid the ink stability.

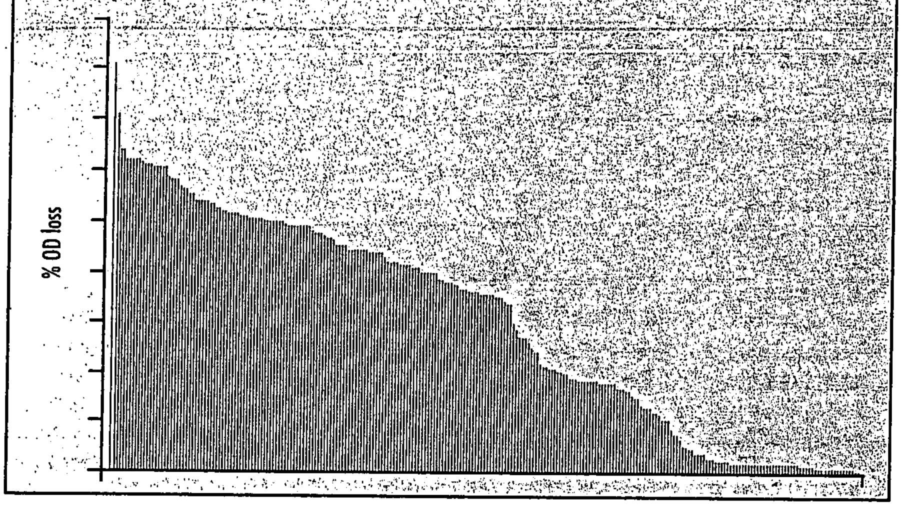
Table 1: Additives to improve ink stability

Additive	Function
Metal chelator, eg EDTA	Prevents M^{2+} (eg Ca^{2+}) from precipitating dyes
Biocide	Prevents bacterial growth
Buffer	Maintains optimum pH Prevents hydrolysis reactions and dye precipitation

Challenges facing aqueous dye-based inks

As mentioned previously, one of the main deficiencies of aqueous inks is the photographic media performance for the digital photographic market. Pigments, which have excellent permanence in terms of stability towards fading by light and ozone, do not penetrate the media surface and so the gloss of the images is compromised. Dyes, on the other hand, provide images with very good print quality and no gloss issues. However, there tends to be a compromise between dyes that are bright but not very light or ozone fast, and dyes that have a smaller colour gamut but generate images that have extremely good permanence.

Figure 7: Graph illustrating the ozone-fastness of a range of cyan dyes



It must also be stressed that the permanence of each dye is directly dependent upon the structure of the substrate onto which it is printed and the conditions under which the image is stored. In recent years there has been a drive towards the use of microporous media in preference to swellable polymer materials for photographic inkjet applications. The use of aluminas and silicas in microporous media provides substrates that look and feel like traditional photographs and deliver rapid drying characteristics enabling fast printing. Unfortunately, it would appear that it in most cases the permanence of dyes is reduced when they are placed on substrates of this nature.

The challenge to ink developers is therefore to develop inks that deliver a high-colour gamut, but where the images have improved light and ozone stability. The majority of the research is focussed on designing new dyes that will deliver both of these properties, with novel chromophores being developed and existing ones being adapted to improve performance on microporous media. Figure 7 illustrates the improvements made to a range of cyan dyes in stability towards ozone, whilst maintaining the correct chroma and correct shade. The graph shows the percentage OD loss from a series of prints all prepared at the same colour depth and exposed to a set amount of ozone.

The other approach to improving the fade resistance of the dyes is to add specific additives to the ink. The exact mechanism of fading is unknown in most cases, but it is believed that most fading processes involve oxidation of the chromophore either via free radical processes or by the interaction of the dye with species such as singlet oxygen. In some cases, depending upon the substrate composition and the nature of the dye, the fading mechanism could also involve a reduction process.

Therefore, there are a variety of additive types which could be included in the ink in an attempt to prevent fading. As UV light is believed to be more damaging than visible light, the additives could be UV absorbers or quenchers such as 2-hydroxyphenyl benzophenones or metal salts. Antioxidants such as hindered phenols could also be added to intercept the oxidative processes.

Two examples of additives improving the lightfastness of dye-based inks are illustrated in Figure 8.[25,26] This approach is extremely difficult to deliver as the effectiveness of the additives will depend on the fading mechanisms for each dye and media type, as discussed above, but will also depend upon the location of the additive relative to the dye once deposited from the ink.

The other main challenge facing aqueous dye-based inks is that, as the dyes are all water-soluble, the waterfastness of the images generated on plain paper is not good. Papers specially designed for inkjet applications tend to contain mordants such as calcium or quaternary amines that insolubilise the dyes. However, inks need to

Figure 8a: Effect of additives on the lightfastness of images formed from magenta

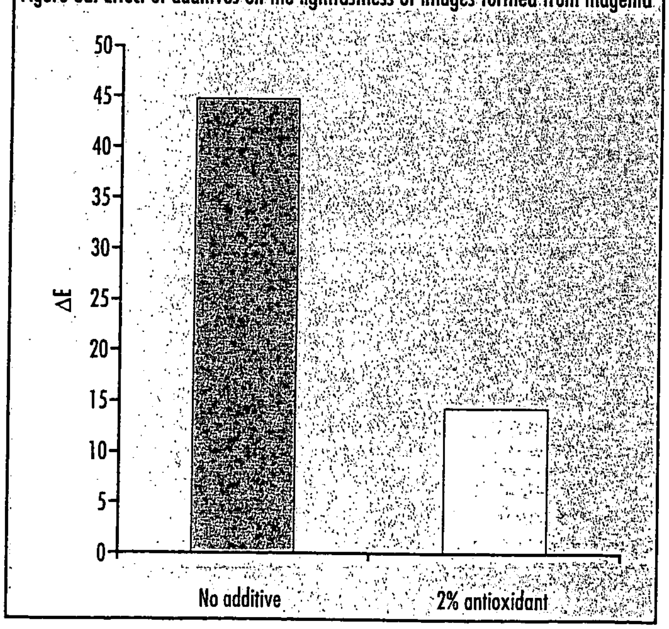
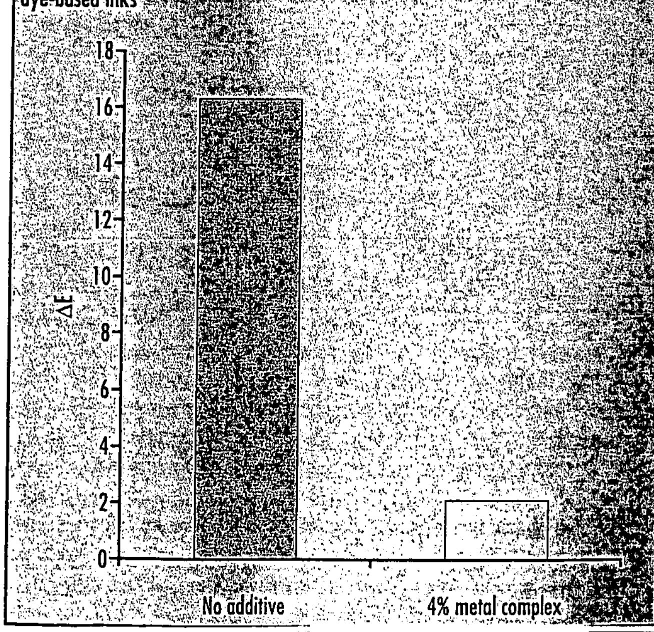


Figure 8b: Effect of additives on the lightfastness of images formed from black dye-based inks



be developed that display good substrate versatility and as such will provide good print performance on a variety of substrates, including cheap non-inkjet paper

In order to provide prints with good resistance to water, the dye or the ink has to be adapted specifically to reduce the solubility of the dye once the ink has been printed. Three of these options are:

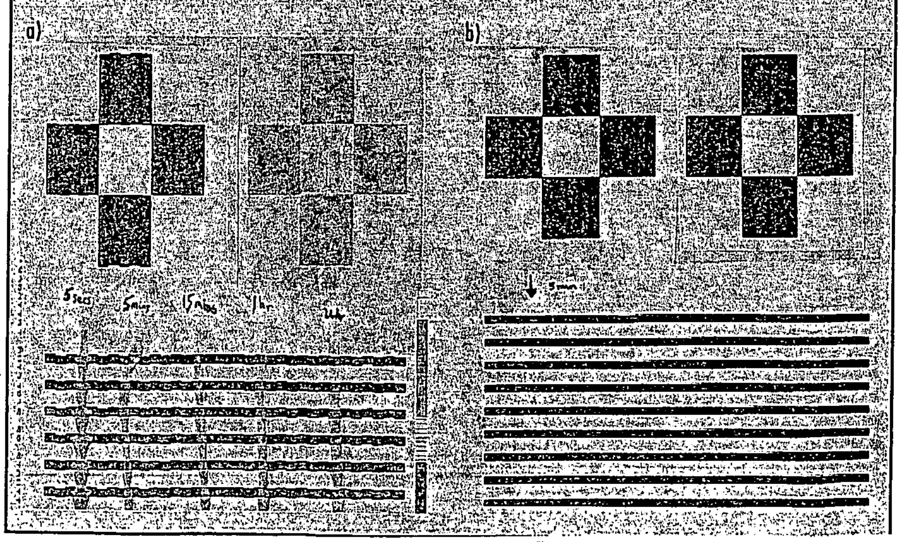
1. Waterfast prints can be achieved through the use of dyes whose solubility is extremely pH-dependent: at the pH of the ink, usually pH 8 to 9, the dyes tend to be very water-soluble, whereas on the paper where the pH tends to be less than 7, the aqueous solubility is minimal. Dyes that can display this pH switch either contain aromatic carboxylic acids instead of sulphonic acids, or contain amines that can form insoluble salts with the sulphonic acids. Figure 9 illustrates prints generated from dye A that contains only sulphonic acid solubilising groups, and dye B that contains protonatable amines and sulphonic acids. The four squares in the top right-hand corner of each set of prints have been soaked in water and it can be clearly seen that much less colour is removed from the print of dye B compared with dye A – the four squares on the left-hand side of each print [(a) and (b)] have not been exposed to water. It can also be observed that when water is run down the series of lines, the transfer of colour is quite visible for dye A, whereas no dye is transferred in the case of dye B.
2. It is also possible to improve the waterfastness of aqueous-soluble dyes by the inclusion of certain water-soluble amines and ammonium carboxylate salts in the inks. In the ink, the amine is unprotonated, but once it is printed, ammonia can evaporate from the surface leaving the free acid which protonates the amine. If correctly chosen, this protonated amine can then form an insoluble salt with the sulphonic acid groups on the dye.
3. Finally, one of the simpler ways to improve the water durability of dyes is by the use of a fixing agent such as a metal salt or a protonated amine.[27] In this case, the fixing agent is applied to the substrate from an additional printhead just before the dye-based ink. This technique can be very effective if the extra complexity and cost of an additional printhead can be incorporated into the printer.

The alternative path to developing an ink solution that will deliver both plain and photographic paper performance is to enhance the properties of pigment-based inks. In this case, the challenge is to create pigment dispersions with colour gamuts that match those of dyes without impacting the gloss of photographic media. Attempts are being made to do this by reducing the particle size of the pigments. However, care has to be taken to ensure that the particle size is not reduced to such an extent that ink stability is compromised by encouraging crystal growth or flocculation of the pigments, or that image permanence properties are adversely affected.

The other issue with pigment-based inks is the durability of the images formed on plain paper in terms of rub and smear fastness. As the pigment particles tend to sit on the surface of the media, they can be easily removed by abrasive forces. In order to avoid this, a polymer needs to be incorporated into the ink to 'bind' the particles together so that the images are more robust. However, adding polymers to inks can result in serious jetting problems due to the increase in viscosity of these solutions.

As can be seen from the above discussion, the formulation development of aqueous inks is far from simple and the strategy adopted is clearly dependent upon the requirements of the application.

Figure 9: Effect of water on a) a dye containing sulphonic acid solubilising groups and b) a dye containing amines and sulphonic acids



Conclusions

Advances in printhead technology mean that inkjet technology can now be used for a variety of applications, ranging from text and photo printing to the preparation of printed circuit boards and displays. To enable the exploitation of inkjet technology within these applications, formulations which are different from and much more complicated than the early inkjet inks have been developed.

Major challenges to ink developers lie ahead as the printhead manufacturers push to develop the technology to deliver smaller droplets so that greater print resolution can be realised, and to allow these droplets to be jetted faster, enabling enhanced printing speeds to be achieved.

In addition, as more applications become available to inkjet, novel ink design will be required to deliver the required performance both in the printhead and on the substrate of choice. Ideally, if developers of inkjet technology are to be successful, it is clear that the ink, printhead and media manufacturers will have to work closely together to deliver acceptable solutions.

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Hawley's

Condensed Chemical

Dictionary

TWELFTH EDITION

Revised by

Richard J. Lewis, Sr.

VNR VAN NOSTRAND REINHOLD COMPANY

New York

the rate of weight change also is measured electronically by taking the first derivative of the weight change with time.

"Thermoguard" [*M & T*]. TM for antimony-based materials for incorporation in PVC and other chlorine-containing plastics for flame-proofing properties.

thermometer. An instrument for measuring temperature. The liquid-in-glass thermometer consists of a graduated glass tube and a bulb containing a suitable liquid whose expansion and contraction indicate the temperature. Its range is from −130 to 600C. For scientific purposes, the most widely used liquid is mercury down to its freezing point at −40C; below this, alcohol gives readings to −100C and pentane to −130C. Colored alcohol is generally used in household thermometers. Mercury thermometers ranging up to 600C are available; the mercury is prevented from vaporizing by a pressurized inert gas inserted above the mercury column. Metal protection tubes for stem and bulb are necessary. The softening point of the glass is of primary importance; borosilicate glasses are satisfactory up to 500C, but Jena glass is required for higher temperatures. Minimum and maximum thermometers are so made as to retain their lowest and highest readings indefinitely; the latter are used for oil-well and other geothermal measurements.

There are several other types of thermometers: (1) Gas, in which either the pressure at constant volume or the volume at constant pressure measures the temperature; these are used for extremely accurate thermodynamic determinations. The gases used are helium, nitrogen, and hydrogen. (2) Bi-metallic, in which the sensing element consists of two strips of metals having different expansion coefficients; its range is from −185 to 425C. (3) Thermoelectric (thermocouple), in which measurement is made by the electromotive force generated by two dissimilar metals; its range is from −200 to 1800C. (4) Resistance, in which temperature is measured by change in the electrical resistance of a metal, usually platinum; its range is from −163 to 660C. (5) An optical fiber thermometer developed by NBS Center for Chemical Engineering has a range of up to 2000C. It is made from a single crystalline sapphire and is much more accurate than the existing standard. Based on fundamental radiation principles, it measures thermodynamic temperatures directly.

See also thermocouple; bimetal.

thermonuclear reaction. See fusion.

thermoplastic. A high polymer that softens when exposed to heat and returns to its original condition when cooled to room temperature. Natural substances that exhibit this behavior are crude rubber and a number of waxes; however, the term is usually applied to synthetics such as polyvinyl chloride, nylons, fluorocarbons, linear polyethylene, polyurethane prepolymer, polystyrene, polypropylene, and cellulosic and acrylic resins.

See also thermoset.

thermoset. A high polymer that solidifies or "sets" irreversibly when heated. This property is usually associated with a cross-linking reaction of the molecular constituents induced by heat or radiation, as with proteins, and in the baking of doughs. In many cases, it is necessary to add "curing" agents such as organic peroxides or (in the case of rubber) sulfur. For example, linear polyethylene can be cross-linked to a thermosetting material either by radiation or by chemical reaction. Phenolics, alkyds, amino resins, polyesters, epoxides, and silicones are usually considered to be thermosetting, but the term also applies to materials where additive-induced cross-linking is possible, e.g., natural rubber.

THF. Abbreviation for tetrahydrofuran.

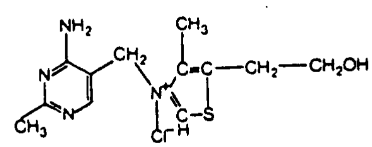
thia-. Prefix indicating the presence of sulfur in a heterocyclic ring.

thiabendazole. (4-[2-benzimidazolyl]thiazole). CAS: 148-79-8. $C_{10}H_7N_3S$.

Properties: White to tan crystals; mp 304C; slightly soluble in water, alcohols, and chlorinated hydrocarbons; soluble in diethylformamide.

Use: Fungicide effective on citrus fruits, anthelmintic.

thiamine. (vitamin B_1). $C_{12}H_{17}ClN_4OS$. (3-(4-amino-2-methylpyrimidyl-5-methyl)-4-methyl-5, β-hydroxy-ethylthiazolium chloride). The antineuritic vitamin, essential for growth and the prevention of beriberi. It functions in intermediate carbohydrate metabolism in coenzyme form in the decarboxylation of α-keto acids. Deficiency symptoms: emotional hypersensitivity, loss of appetite, susceptibility to fatigue, muscular weakness, and polyneuritis.



Sources: Enriched and whole-grain cereals, milk, legumes, meats, yeast. Most of the thiamine commercially available is synthetic.

Use: Medicine, nutrition, enriched flours. Iso-

塗工技術概論
—20世紀の紙塗工技術変遷—

Kami Pa Gi Kyoshi / Japan TAPPI Journal

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A Review of Paper Coating
—Paper Coating Technologies in the 20 th Century—

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Production of coated papers for graphic arts reached 6.73 M tons in 2000 in Japan. It has been continuing to expand since the production started in 1910 s.

In this paper, the history of coating methods and coating materials are described with divided into 5 periods ; (1) Brush and Air knife coating in the period from 1910 s to 1960 s, (2) On-machine coating in the 1950 s and 1960 s, (3) High speed blade coating in the 1970 s and after, (4) Light weight on-machine coating by Gate roll coater in the 1980 s and after, (5) Double blade coating in the 1990 s.

It is obvious from the facts that both the coating methods and the coating materials have been continuing to evolve to match the market demands and to obtain high productivity, and it will continue in the future.

Keywords：ブラシコータ，エアナイフコータ，ブレードコータ，ゲートロールコータ，ラテックス，カオリン，炭酸カルシウム，塗工技術，アート紙，コート紙，塗工紙，微塗工紙
分類：N_1 塗工・塗工機一般，N_2 塗料調成，N_3 塗工機

1. はじめに

2000年の印刷用塗工紙（塗工印刷用紙＋微塗工印刷用紙）の国内生産量は673万トンを記録し，過去最高となった。これは，いわゆる情報産業の拡大に伴う旺盛な国内需要に支えられた結果である。一方で，情報産業は紙の将来を大きく左右すると考えられ，今後の紙のあり方に対する不安を残しながらも，紙の消費は伸びつづけた形で20世紀を終えた（図1[54)]）。今回，紙塗工技術概論というテーマを頂いたのを機会に，19世紀後半に海外でスタートし，20世紀に入って日本でも開始された工業としての紙塗工に関し，塗工方法とそれに伴う塗工材料を中心にした塗工技術の変遷に触れてみたい。

塗工紙の生産は，当初アート紙だけであり，高級印刷向け加工紙を製造するための抄紙から独立した特殊作業とみなされていた。その後，1950年代のオンマシンコーティングの開始と共にコート紙が出現し，現在まで，いくつかのグレードに分かれながら拡大を続けてきた。ここでは，①紙塗工開始からアート紙全盛時代（1910年代～1960年代），②オンマシンコーティングの出現とコート紙の成長（1950年代，1960年代），③軽量コート紙の成長と高速ブレードコータ化（1970年代およびそれ以降），④微塗工紙の出現とその急成

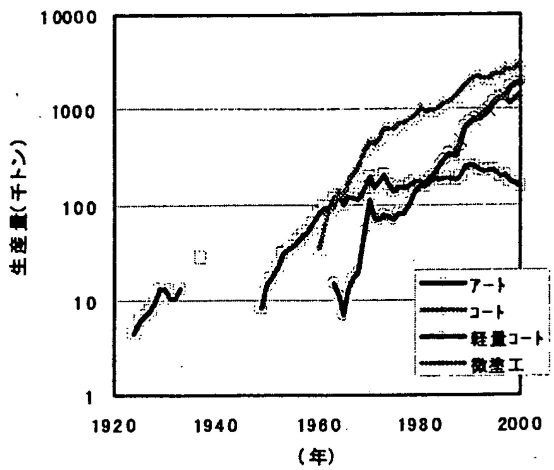

図 1　塗工紙生産量推移

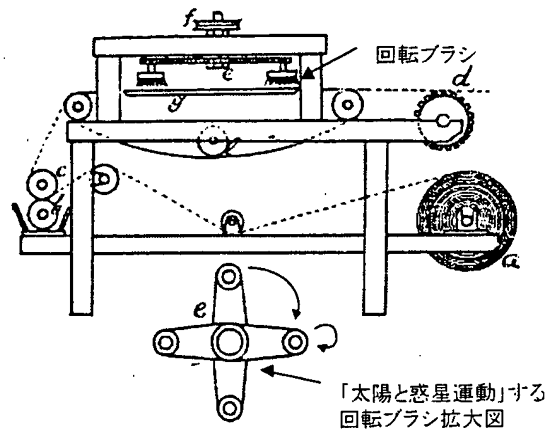

図 2　フランス式回転ブラシコータ

長（1980年代およびそれ以降），そして，⑤ブレードダブル塗工による高品質化（1990年代）の年代に分けて，その時期に使用された主要な塗工装置や塗工材料ついて述べる。

なお，筆者は製紙メーカで印刷用塗工紙の製造に関わっている技術者であり，ここでは，紙塗工技術＝印刷用塗工紙の顔料塗工技術であることをご容赦願いたい。また，本報告では，特に断りがない限り，印刷用の顔料塗工された紙全体を塗工紙と表現し，アート紙，コート紙は塗工紙のグレードを示す言葉とした。また，年代を含む技術変遷については，過去に発表された総説を中心に引用しており，個別に引用個所を示すことは難しいので技術変遷引用文献としてまとめて記し，個別技術については通常どおり引用個所にその文献を示す。

2　紙塗工開始からアート紙全盛時代（1910年代～1960年代）

2.1　紙塗工開始とブラシコータ

紙に顔料塗工する目的は，印刷適性と外観を改善することであり，フォードリニア抄紙機が開発された約50年後の1850年代にブラシコータが壁紙の製造に使用されたのが始まりとされている。塗工紙の製造は，ブラシコータの開発により工業的生産規模となり，初期のものは，「太陽と惑星」運動する回転ブラシが使用されていた（図2[1]）。日本では，1878～1880年頃印刷局抄紙部にロールタイプの片面コータがドイツより輸入され，壁紙や革紙などを製造したのが記録に残っている最初のものである。

アート紙（この時期はアート紙＝塗工紙）は，1900年頃より輸入されていたが，第一次世界大戦勃発により輸入品が希薄になる中，国内需要が高まり，1915年に水野倶吉，井口誠一の共同事業として日本アート紙合名会社が設立され，国内での製造がスタートする。アート紙の工業的生産は，日本加工製紙（日本アート紙合名会社を母体として1917年設立）と三菱製紙が相前後してロールタイプの片面ブラシコータを米国より輸入して開始された。日本加工製紙は，王子工場に54インチ（1,372 mm）のコータ3台を1919年から順次稼動させ，三菱製紙は高砂工場に46インチ（1,168 mm）のコータ1台を1918年に稼動させている。また，富士製紙は，神崎工場に65インチ（1,651 mm）と53インチ（1,346 mm）のコータ各1台を同じく米国より導入し，1922年にアート紙の製造を開始した。

国内でのアート紙製造が製造業として安定したのは，輸入アート紙に高率の関税が課せられたこと（1926年）によると言われている。その後，1933年に北越製紙市川工場でも生産が開始され，1937年が戦前の最盛期で生産量27,200トン/年であった。戦争により各社生産の中断を余儀なくされただけでなく，大きな被害を受けた工場もあったが，1946年末にはアート紙の生産が再開された。

ブラシコータには，上記したロールタイプの片面機（図3[2]）と水平タイプの片面機，両面機（図4[2]）があ

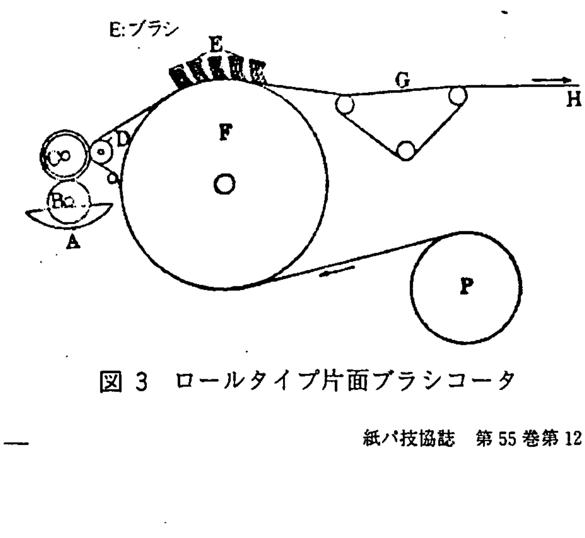

図 3　ロールタイプ片面ブラシコータ

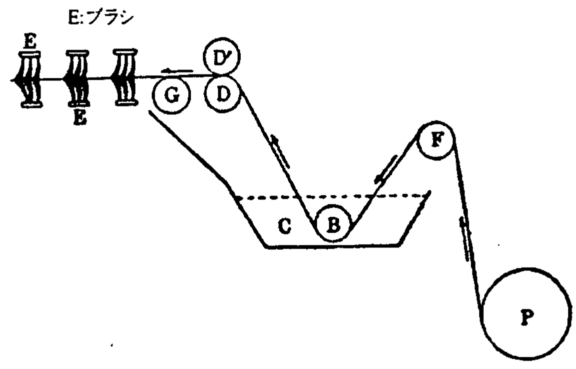

図 4　水平タイプ両面ブラシコータ

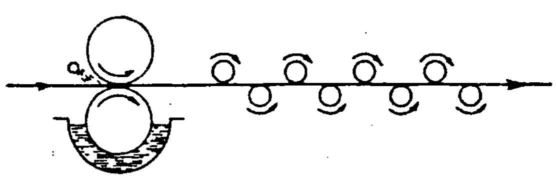

図 5　スプレッドシャフトコータ

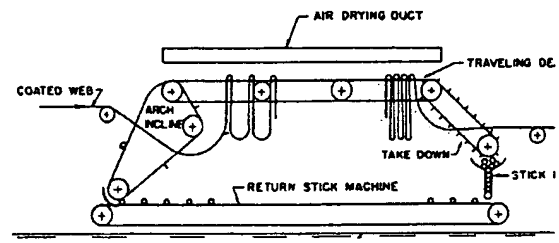

図 6　フェスツーンドライヤ

ったが，国内では専ら片面機が使用され，塗工速度は60〜70 m/分（1935 年頃）であった。最初のブラシは粗い剛毛から作られて固定されており，その後順次柔らかい毛のブラシが使用され，半数以上のブラシが左右に摺動して塗料をならした。なお，塗工量はアプリケート量で決定される。

欧米では，両面ブラシコータやそのブラシを 10 cm 程度のリバースロールに置き換えたスプレッドシャフトコータ（図 5[5]）も使用され，国内では，三菱製紙が，消耗が激しくかつ刷毛目が出易いブラシの代わりに軟質ゴム製ドクターで平滑化するコータを開発し，これで生産された塗工紙は，原色印刷用に使用されたと言われている。なお，両面機は，富士製紙神崎工場で 65 インチ（1,651 mm）のものが，1923 年にドイツより輸入されたが，操業上の課題が多く，1927 年に片面機に改造された。

1959 年の文献[5]に，米国で当時わずかに残っていたとされる高級塗工紙製造用のブラシコータが紹介されており，ブラシコータの最終段階と考えられるその能力は，塗工速度 61〜107 m/分，塗料濃度 35〜45%，塗工量範囲 13〜30 g/m^2 と記載されている。

塗工材料では，国内産クレーと硫酸バリウムが顔料として当初使用され，その後サチンホワイトや軽質炭酸カルシウムが併用されるようになって光沢や印刷適性が向上した。接着剤としては主にカゼインが使用され，オフセット印刷に必要な耐水性は，サチンホワイト，ホルマリンやヘキサメチレンテトラアミンのカゼインに対する硬化耐水化によって得ていた。表 1[1]に 1935 年頃のブラシコータ配合例を示す。

ブラシコータに組み合わされた乾燥方法は，フェスツーン（Festoon）ドライヤ（図 6[33]）である。これは，塗工後，下から持ち上がって来る棒にループ状に紙が引っ掛けられ，その状態で 27〜65℃ の乾燥室を 10〜20 分掛けて移動しながら乾燥させる方法である。乾燥終了後，棒が外れて紙は巻き取られ，棒は回収される。

2.2　エアナイフコータ

S.D. Warren 社の Terry らによってエアナイフコータ（図 7[30,33]）が 1938 年に完成した。このことにより塗工速度は 100 m/分を超えるようになっただけでなく，原紙に対する品質要求が大幅に減った。すなわち，ブラシコータでは，塗料が原紙に供給された後何度もブラシでしごかれるため原紙に高い耐水性が要求されたのに対し，エアナイフコータによる塗工は，原紙上に過剰に供給された塗料が原紙と接触直後より脱水され，原紙に近い不動化（フィルタケーキ）層と原紙から離れた流動性を有する 2 つの層となり，流動性を有する層をエアナイフの風圧で吹き飛ばす方法で行われており（図 8[33]），いわば非接触の計量方法であること

表 1　ブラシコータ塗料配合例（1935 年頃）

光沢アート紙　例 1		光沢アート紙　例 2		半光沢アート紙	
硫酸バリウム	50	クレー	90	クレー	85
クレー	50	サチンホワイト	10	沈降性炭カル	15
カゼイン	12.5	カゼイン	17	カゼイン	17
蝋石鹸	1	蝋石鹸	1		

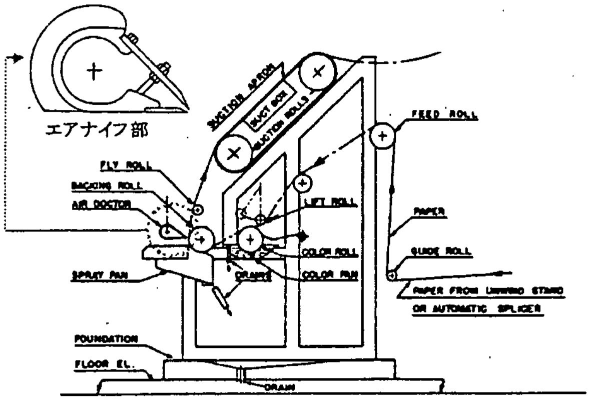

図 7　エアナイフコータ（USP 2,139,628）

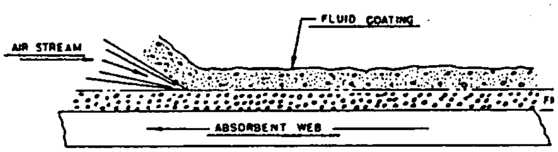

図 8　エアナイフコータでの計量機構模式図（フィルタケーキ理論）

による。

ブラシコータの塗料はそのままエアナイフコータに利用できたこともあり，国内では，1955 年～1960 年がブラシコータ＋フェスツーンドライヤの組み合わせからエアナイフコータ＋トンネルドライヤの移行期であった。この方式転換により，1960 年には当時のアート 3 社（三菱製紙，日本加工製紙，神崎製紙）の生産量は合計で年間 8 万トンになった。

2.3　ブラシコータ，エアナイフコータ用の塗工材料と塗料流動特性

塗工材料では，国内において 1950 年頃にアート紙用の接着剤としての澱粉変性が積極的に検討されたが[55]，耐水性などが課題となり一部の使用に留まった。ラテックスは，1950 年代前半にカゼインの代替と合成樹脂主体の塗料を塗工する樹脂コーティング用を目標として，戦後国内で唯一調達できた塩化ビニリデン系樹脂で研究が行われ，塩化ビニル・塩化ビニリデンラテックスが 1954 年頃一部使用された。その後，1957 年頃にダウラテックス 512 R（スチレン・ブタジエンラテックス）や ICI のブタコン ML 501（ブタジエン・メチルメタクリレートラテックス）などの輸入ラテックスが導入され，エアナイフで塗工したアート紙においてラテックスが初めて本格的に使用された。また，この時期，防腐剤，消泡剤やスーパーカレンダーのダスティング防止剤としてのステアリン酸カルシウムなどの助剤が使用され始めた。

接着剤では，さらにその後（1966 年）のカゼイン価格高騰（表 2[40]）に伴い，大豆タンパク[57]，ポリビニルアルコール（PVA）やカゼインと相溶性が良好な水溶性ポリマー[58]が検討された。特に，PVA は当時比較的安価（200～250 円/kg[40]）に入手できた合成材料であってしかも接着強度が強く，その結果得られる塗工紙の白色度や光沢が高いことから（図 9[56]）大きく期待され，積極的に検討された[56,59～61]。しかしながら，PVA を配合した塗料は高せん断速度下での粘度が高く，エアナイフコータやトランスファロールコータ（後述）で塗りムラが発生すること，当時求められたレベルの耐水性付与が難しいことなどにより，結局，PVA は広く使用されるようにはならなかった。

一方，リン酸エステル化澱粉が 1960 年代後半に紹介され[62,63]，これは従来の澱粉では難しかったサチンホワイトとの混和性が良好でしかもサチンホワイトとの反応で耐水性が発現するのでカゼイン代替として受け入れられ，現在も使用されている。

塗料の流動特性については，1916 年に Bingham が

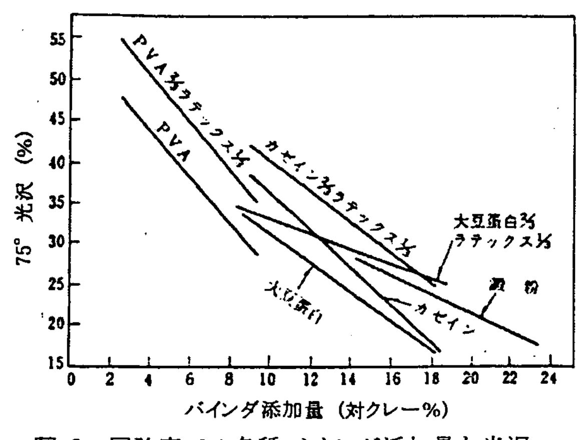

図 9　同強度での各種バインダ添加量と光沢
コート量：22 g/m^2，ラテックス：ダウ 612，カオリン：HT

表 2　1965 年前後のカゼイン価格の動き

年	1962	1963	1964	1965	1966 前半	1966 後半	1967 前半
価格(円/kg)	175～180	170～180	160～165	160～185	280～330	220～250	250～260

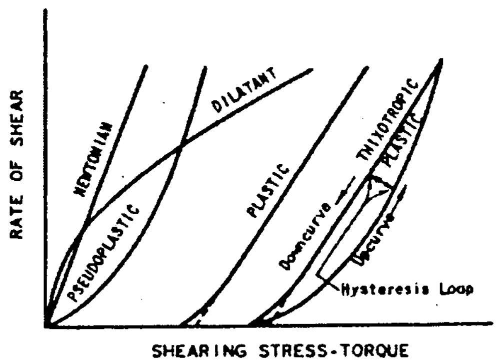

図 10　回転粘度計で得られる各種流動特性

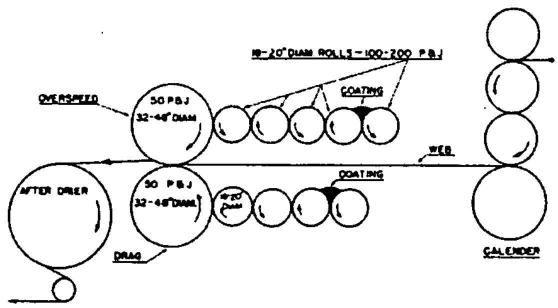

図 11　マッセイコータ（USP 1, 921, 369）

プラスチックフロー（plastic flow/塑性流動）に関する考えを報告しており，現在でも広く利用されている回転ボブとカップからなる高せん断粘度計が1940年代から1950年にかけて開発され[64~66]，シュードプラスチックフロー（pseudoplastic flow/擬塑性流動），チキソトロピー（thixotropy），ダイラタンシー（dilatancy）などの現象が理解された（図10[64]）。

この時期の塗料の流動特性と塗工適性や仕上り品質の関連として，ブラシコータやエアナイフコータでは，塗工面の平滑化（レベリング）に関してニュートニアンな流動が好ましく，例えば，プラスチックフローの塗料では最初の硬いブラシでは塗料が流動性を示して平滑化できるが，毛が細い仕上げブラシでは塗料が流動性を示さず刷毛目を残し易いことが知られていた。

3.　オンマシンコーティングの出現とコート紙の成長（1950年代，1960年代）

3.1　トランスファロールコータ

オンマシンコーティングは，マシンのドライヤ中間部あるいはカレンダー後に塗工装置を設けたものであるが，それまで，抄紙とは別の特殊作業（加工）と見なされていた塗工が抄紙と同じ速度で可能となった技術進歩を示すだけでなく，この時期に実用化されたトランスファロールコータは，ブラシコータやエアナイフコータに要求された塗料とは異なる塗料物性（高濃度で低粘度等）を要求し，塗工材料も大きく変化した。

最初のトランスファロールコータは，1933年に開発されたマッセイ（コンソリデーテッド）コータ（図11[28]）である。これは，印刷機のインキ練りおよび分配を担う多段ロール方式を取り入れたもので，印刷商であったピータ　マッセイが当時まだ塗工紙を手がけていなかったコンソリデーテッド社と出会うことで完成された。また，この時期米国ではヒートセットレタープレスが開発され，オンマシンコーティングとの組み合わせにより，出版用塗工紙（Magazine grade あるいは Publication grade）の大量生産と雑誌の大量発行が可能となった。タイム社から1936年に発行されたライフ誌にマッセイコータでオンマシン塗工した中質塗工紙が採用され，ライフ誌を魅力あるものにしたことは良く知られている。トランスファロールコータによるオンマシンコーティングは，マシンの操業性を損なうことなく塗工できるコータとして，その後KCM（キンバリー・クラーク・ミード）コータ（図12[28]），ウェストバージニアコータ，セントレジストファーバコータ，チャンピオンマシン（ハミルトンロール）コータ（図13[28]）など多くのトランスファロールコータが開発された。

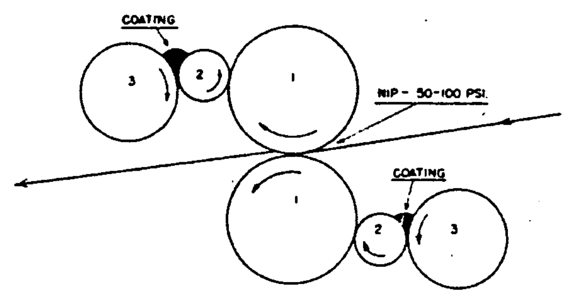

図 12　KCM コータ（USP 2, 647, 842）

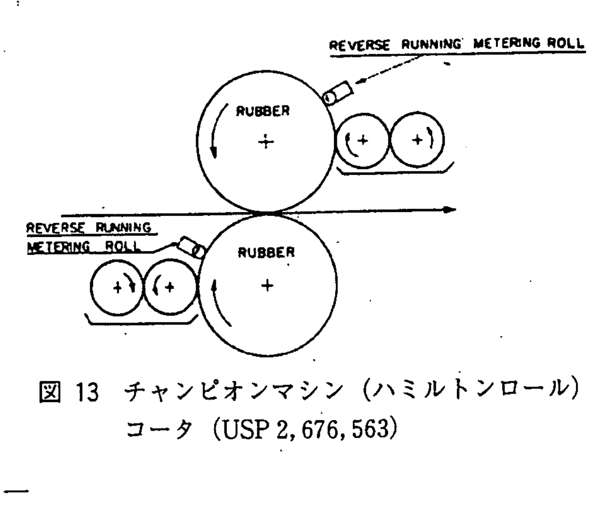

図 13　チャンピオンマシン（ハミルトンロール）コータ（USP 2, 676, 563）

3.2　トランスファロールコータ用の塗工材料と塗料流動特性

トランスファロールコータでの両面塗工では，コータを出てからシリンダドライヤに紙が達するまでに，塗料がべたつかない程度に乾燥するような60%以上の高濃度塗料を要求しただけでなく，各ロールに塗料が均一に転移し，かつミスティングが発生しないようなチキソトロピー（ヒステリシス）度合いが大きいプラスチックフローの塗料が望まれた。

このため，米国において1930年代後半より40年代にかけて，粘度が高く塗料の高濃度化が難しい英国カオリンに代えて，当時ゴムやセラミックにしか利用されていなかった米国産カオリンを紙塗工に利用することが検討された。1949年には塗工用カオリンとしてNo 1～No 4（ただし，No 4は壁紙用）のグレードが準備されるとともにスプレードライの予備分散品の生産が開始され，1950年代前半には高濃度カオリンスラリーが生産された。その後，1961年に高度浮遊選鉱と磁気選鉱による白色度90%グレード品，1962年，1965年にデラミネーテッドカオリンの製法特許成立，そして1964年の焼成カオリンの出現へと，1950年代から1960年代初めにカオリンの精製・製法技術が大きく進歩し，その機能化が進んだ。その結果，1960年にはNo 1～No 4のグレードだけであった塗工用カオリンが，1970年にはプレミアムの高白品やデラミネーテッド，微粒高光沢，焼成などの多くのグレードがラインアップされた（表3[43]）。

また，米国での接着剤の流れとしては，当初は膠（animal glue）が使用されていたが，品質が安定しないことと紙が不快臭を持つことが問題であり，1895年頃よりカゼインが使用され始めた。一方，カゼインに代えて澱粉を利用することも精力的に検討され，1900年頃に酸化澱粉が開発されたが，耐水性が乏しいことが欠点であり，尿素ホルムアルデヒド樹脂，メラミンホルムアルデヒド樹脂などによる耐水化処理法が開発されたのが1930年代終期である。1950年代前半に澱粉の酵素変性技術が確立され，これによって工場で求められる粘度に変性できるようになり，ロールコータ用の接着剤として多量に使用され始めた。その後1950年代半ばにエーテル化澱粉が紹介され，1960年代[67]には澱粉の連続熱化学変性システムが開発された。また，ロールコータ特有の流れ筋やオレンジピールの発生度合いと塗料の流動特性の関係も検討され，パターンがきつい濃度55%以上のカゼイン塗料ではダイラタンシー傾向を示すプラスチックフローであり，パターンが小さい澱粉系塗料ではチキソトロピー度合いが大きなプラスチックフローを示すことから，ロールコータでのパターン発生の少ない塗料の評価指標として，チキソトロピー度合いを数値化したレベリングインデックスが導入されたりした[64]。ラテックスについては，1944年に「白土，澱粉，エステルゴムエマルジョン」に関する特許（USP 2,355,953）が成立し，1947年にスチレン・ブタジエンラテックスが市場に現れた。

表 3　塗工用カオリンのグレード（米国/1960年と1970年）

	1960年		1970年	
	白色度（%）	2 μm以下（%）	白色度（%）	2 μm以下（%）
No. 1 プレミアム	—	—	90	93
No. 1 標準	87	93	87	93
No. 2 プレミアム	—	—	90	80
No. 2 標準	86	80	86	80
No. 3	85	73	85	73
高光沢プレミアム	—	—	90	98
高光沢標準	—	—	86	95
デラミネーテッド微粒	—	—	87	97
デラミネーテッド標準	—	—	88	80
超微粒子	—	—	88	95
焼成品	—	—	86～90	60～90

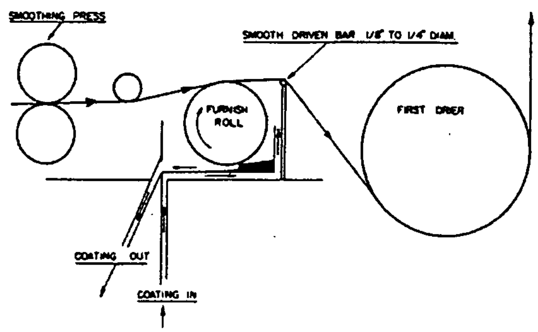

図 14　チャンピオンロッドコータ
(USP 2, 229, 621)

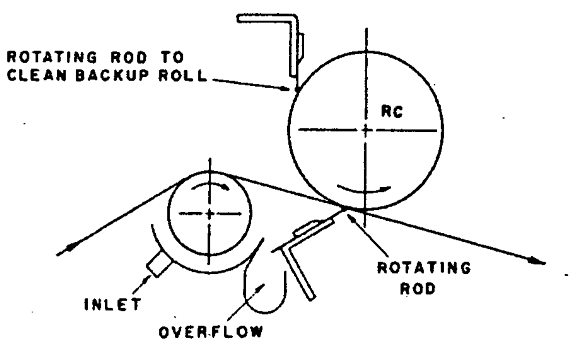

図 15　チャンプレックスコータ

3.3　国内のオンマシンコーティング

国内でのオンマシンコーティングは，米国でのトランスファロールコータを中心したものとは異なる形でスタートした。すなわち，1950 年に本州製紙がチャンピオンロッドコータ（図 14[28]）で，十条製紙がオフセットグラビアコータでオンマシンコーティングによる塗工紙の生産を開始した。しかし当時は，オンマシンコーティングに適するクレーがなかったこと，また，米国ではこの時期凸版印刷用の出版用紙需要が高く接着剤に澱粉を使用することができたのに対し，国内では接着剤にカゼインを使用せざるを得なかったことやアート紙並みの品質を要求されたため，当初は操業上，品質上での苦心を要したと言われている。

オンマシンコーティングによる品質向上策として，ダブルコーティングが 1960 年に神崎製紙で始められた。これは，下塗りにハミルトンロールコータを，上塗りにチャンプレックスコータ（図 15[31]）を採用することで塗工量を増やし，アート紙に近い品質を得た。同じ頃，日本加工製紙がオフマシンのフレキシブレードコータ（後述）で，本州製紙がエアナイフコータで，神崎製紙とともにいずれも名称に「コート」が付く塗工紙の生産を開始し，アート紙と区別される形でコート紙が定着した。1960～1965 年の間に塗工紙メーカは 11 社となり，コート紙の生産が大幅に増大した（図 1)。

表 4 に，1959 年と 1965 年の文献[5,68]に紹介されている米国のロールコータ用，国内のチャンピオンマシンコーティング（ロッドあるいはチャンプレックス）および国内のブラシコータ，エアナイフコータ用配合例を示す。

4.　軽量コート紙の成長と高速ブレードコータ化（1970 年代およびそれ以降）

4.1　ブレードコータ

多色オフセット印刷が 1960 年代に入って普及し，先のオンマシンコーティングで製造された安価な塗工紙，すなわちコート紙の成功により，多数の上質紙メーカがこの分野に参入するとともに，その塗工方法もロールコータ，ロッドコータやブレードコータなどを単独あるいは組み合わせて，オンマシンやオフマシンで塗工するなどその製造方法が多岐にわたるようになった。また，キャスト紙，アート紙（グロス，マット）およびコート紙（グロス）からなる塗工紙に加えて，1960 年代後半から 1970 年代にマットコート紙，軽量コート紙および中質コート紙が市場に現れた（図 16[69]）。

表 4　各種コータ用塗料配合例（1959～1965 年頃）

	ロールコータ	チャンピオンマシンコーディング		ブラシ，エアナイフ	
	雑誌向け	凸版用	オフセット用	凸版用	オフセット用
クレー	90	100	100	80	66
軽質炭酸カル	10	—	—	20	—
サチンホワイト		—	—	—	34
ワナックス	3	6	5	4	8.5
カゼイン	—	—	12.5	11	16.5
澱粉	11	16	—	—	—
固形分（%）	64	43	42.5	40	

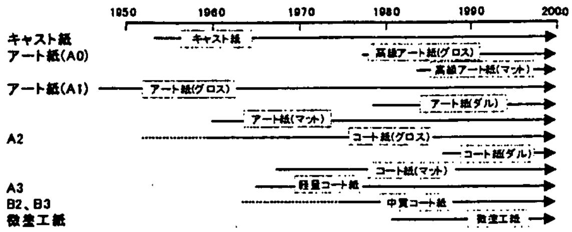

図 16　塗工紙開発の変遷

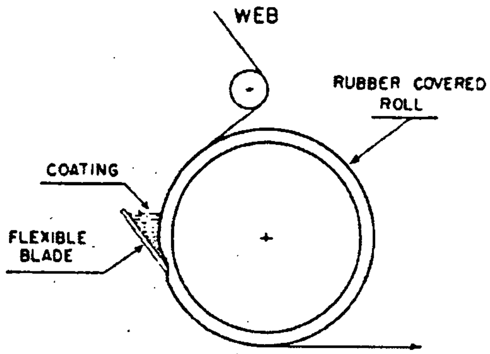

図 17　パドル型ブレードコータ
(USP 2,368,176, 2,593,074, 2,796,846)

ブレードコータは，Tristによって1945年に米国で成立した特許が始まりと言われている。ただし，この内容は，コータデザインに関するものでなく塗料配合に関するものであり，その後機械デザインを記載した特許が成立し，パドル型ブレードコータとして知られている（図17[30]）。この時期のブレードコータには，インバーテッドロールブレードコータ，加圧ポンドを供えたフレキシブレードコータ（図18[30]），フラデッドニップコータ（図19[30]）やファウンテンコータなどがある。Tristのブレードコータは，パン用包装紙のワックス塗工に当初使用され，印刷用塗工紙の製造に使用されたのはBlandin　Paper社が1956年に設置したオフマシンコータが最初である。このとき製造された中質塗工紙は6.5 g/m^{2}の塗工量で，ロールコータで9.8 g/m^{2}塗工したものと同品質と評価され[34]，短期間で出版用として受け入れられた。その後，高速塗工が可能でしかもロールコータ特有のパターンが出ないコータとして急速に普及した。

国内におけるブレードコータの設置ついて，この時期の文献[9,70]）や1967年通産省発行の紙・パルプ工業設備調査報告書によれば，1960年大昭和製紙富士工場に3,,280 mm幅，600 m/分のパドルブレードコータ，1961年日本加工製紙京都工場に1,700 mm幅，300 m/分のフレキシブレードコータ，1962年大昭和製紙吉永吉原工場に2,200 mm幅，410 m/分のインバーテッドブレードコータの設置が記載されており，この辺

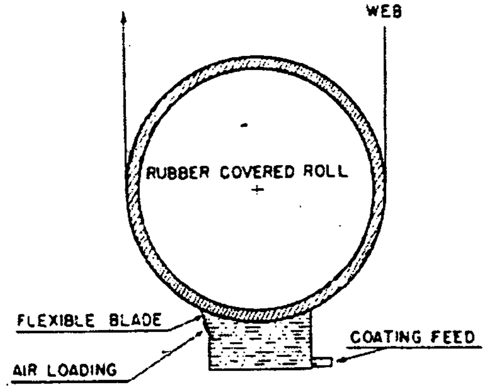

図 18　フレキシブレードコータ
(USP 2,285,531 他)

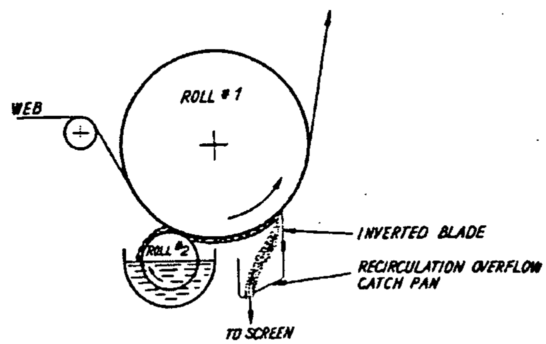

図 19　フラデッドニップコータ

りが，最も早く導入されたブレードコータと考えられる。というのも，当時チャンピオンロッドコータやチャンプレックスコータはブレードコータに分類されており[71]，上記紙・パルプ工業設備調査報告書においても，ここでいうブレードコータとの区別が明確でないことによる。

ちなみに，チャンピオンロッドコータは1930年代に開発され，最も機構が簡単なコータの一つであって，当初は鋼製のブレードナイフが使用されたが，繊維や異物によるスクラッチが発生するため，クロムメッキした回転ロッドが使用されるようになった[31]。

4.2　ブレードコータの高速，広幅化

1950年に国内で開始されたオンマシンコーティング以来，コータはオンマシンかオフマシンかと言う議論がなされていたが，ブレードコータの高速化に伴いその議論に回答が出された。すなわち，ブレードコータの能力として，表5[72]に示すように，1966年の新設エアナイフコータが3.2 m幅，400 m/分であったのに対し，それを遡る1960年設置のブレードコータが3.2 m幅，600 m/分とエアナイフコータの1.5倍のスピードで設計されていた。国内でのブレードコータの幅と速度は，その後1970年代に5 m，1,000 m/

表 5　ブレードコータの高速，広幅化の流れ

設置年月	製品取り幅 (mm)	設計速度 (m/分)	日産 (トン)	平均米坪 (g/m²)		設置会社/工場
エアナイフコータ						
1966 年	3,273	400	116	96	オフ	三菱製紙/八戸
ブレードコータ						
1960 年	3,280	600	113	70	オフ	大昭和製紙/富士
1966 年	3,180	600	137	96	オフ	日本パルプ工業/米子
1971 年	4,800	900	324	102	オフ	三菱製紙/八戸
1971 年	3,390	915	146	85	オフ	王子製紙/春日井
1972 年	3,600	1,200	197	93	オフ	日本加工製紙/高萩
1973 年	5,680	900	276	95	オフ	大昭和パルプ/岩沼
1980 年	5,380	1,050	382	68.3	オフ	神崎製紙/富岡
1984 年	3,150	1,300	191	64.0	オフ	大王製紙/三島
1985 年	5,050	1,200	400	66.7	オフ	王子製紙/春日井
1986 年	5,050	1,000	411	73.8	オン	北越製紙/新潟
1987 年	4,728	1,200	447	87.5	オフ	山陽国策パルプ/岩国
1988 年	5,050	1,500	486	73.9	オフ	三菱製紙/八戸
1991 年	5,280	1,500	511	80.0	オフ	王子製紙/春日井
1997 年	7,040	1,300	700		オン	日本製紙/岩国
1997 年	7,040	1,800	700		オフ	王子製紙/米子

分，1980 年代に 5 m，1,500 m/分となり，1990 年代に 7 m，1,800 m/分と広幅，高速化が進んだ。ちなみに，海外を含む現時点での最大，最速のブレードコータは，1999 年 Asia Pulp and Paper 社の江蘇金東紙業 (Gold East Paper Mill/中国大港 (Dagang)) に設置された 9.7 m 幅，2,000 m/分の 4 ヘッドオフマシンコータであり，同社では，本年同型のものがもう 1 台スタートする予定である。

4.3　高速ブレードコータ用の塗工材料と塗料流動特性

ブレードコータによる高速塗工は，乾燥負荷が小さくなるように高濃度でしかも低粘度の塗料を要求した。このため，塗工材料では，接着剤としてのラテックスの比重がますます高まり，1960 年代後半のカルボキシ変性ラテックスの登場[73,74]は，機械安定性，澱粉との混和性や接着力を大きく向上させ，ラテックスを以前にも増して魅力あるものとした。さらに，印刷光沢や吸水着肉性などを向上させるためのモノマー種の多様化，オフ輪印刷での耐ブリスタ性を付与した低ゲル化，グラビア印刷の着肉性を向上させる低ガラス転移温度 (Tg) 化，各種相反する特性を両立させるための異層構造化，ソールバインダが可能なアルカリ膨潤型化，

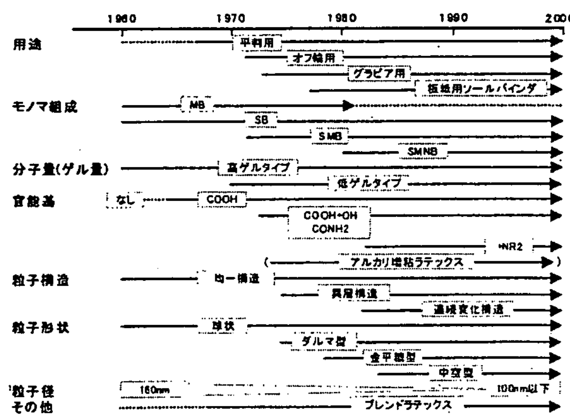

図 20　塗工紙用ラテックスの変遷

接着強度改善と高せん断粘度低減を可能とする小粒子径化などラテックスの機能強化が図られ，また，それぞれのコータに応じたオーダーメイド化が進んだ (図 20[47,51,26])。

塗工材料面でのもう一つの大きな動きは，湿式粉砕した重質炭酸カルシウム (以後，炭酸カルシウムを炭カルと略す) の利用が，中性抄紙と合せて 1980 年代に入って広まったことである。合成品である軽質炭カルは，ブラシコータの時代より使用されており，また，

ヨーロッパでは1960年代後半より湿式粉砕重質炭カルがマット紙や下塗り用に，国内でも乾式粉砕品がマット紙に使用されていた。一方，グロス品に使用できてしかもストリークやスクラッチの原因となる粗粒分を除去した微粒の湿式粉砕重質炭カルは，1970年代後半にその製造技術が確立した[75,76]。重質炭カルは，米国産カオリンよりさらに流動性が良く，しかも不動化濃度が高い（表6[77]）ことから塗料を高濃度化し易い特徴がある。また，重質炭カル塗料は低濃度で塗工するとカオリンと比較して光沢が劣るが，高濃度で塗工すればカオリンと同等レベルまで光沢を改善でき

表 6　カオリンと重質炭酸カルシウムの不動化濃度

	英国カオリン	米国＃2カオリン	重質炭カル
濃度(%)	63.7	70.1	73.8
粘度(mPa·s)	838	500	380
不動化濃度(%)	72.9	75.0	82.1

バインダなし

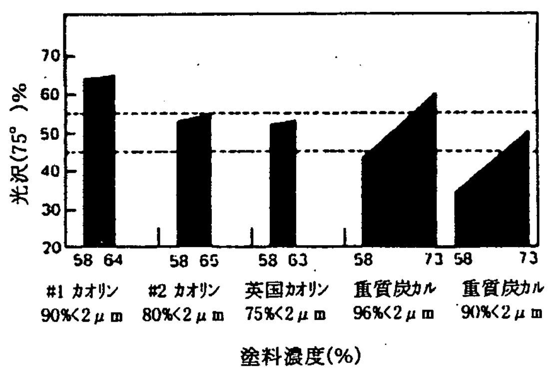

図 21　光沢に対する塗料濃度の影響
（カオリンと重質炭カルの差）

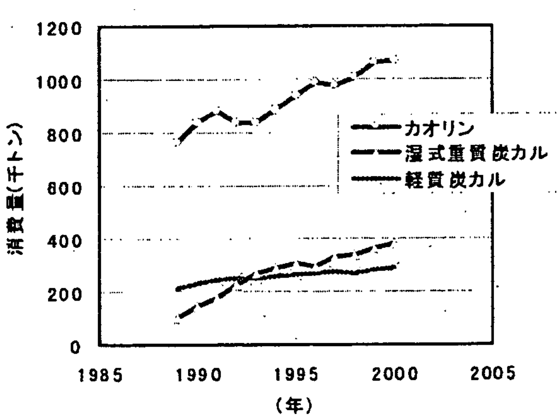

図 22　顔料消費量推移

（図21[78]），高速塗工が可能でしかも乾燥エネルギーを低減できるという特徴がある。なお，湿式粉砕重質炭カルの消費量は，1990年代に入っても，コータの高速化とブレードダブル塗工（後述）に伴い高い伸びを示しており（図22[79]），1989年にはカオリン消費量と比較してその13%であったものが，2000年（見込み）ではカオリン消費量対比その36%となっている。

4.4　ブレードコータの高速化による課題

コータの高速化に伴ういくつかの問題がクローズアップされた。1つは，ストリーク，スクラッチに代表される塗工欠陥の発生であり，もう一つは，バインダマイグレーション（乾燥時の水分移動に伴うバインダの移動）による印刷モットル（印刷ムラ）の発生である。ストリークやスクラッチは，ブレードで計量される際の塗料の流動性不良や塗料中の粗大粒子，脱毛繊維などの混入異物が原因となる。特に，フラデッドニップコータなどのドェル長（塗料供給部からブレードまでの距離）が大きいものでは，塗料が原紙に供給されてブレードで計量されるまでの間に塗料から原紙への脱水が起こり（図23[27]），ブレード直下では塗料濃度が設定以上に高くなっている（図24[80]）ことが流動性不良の原因と考えらる。これは，ストリークやスク

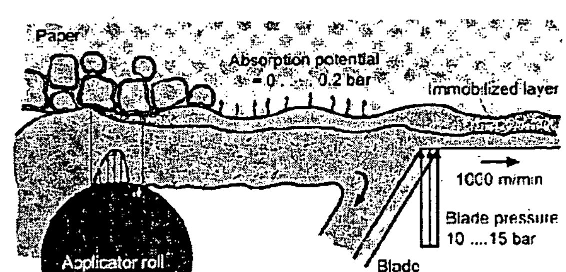

図 23　フラデッドニップコータでの塗料脱水模式図

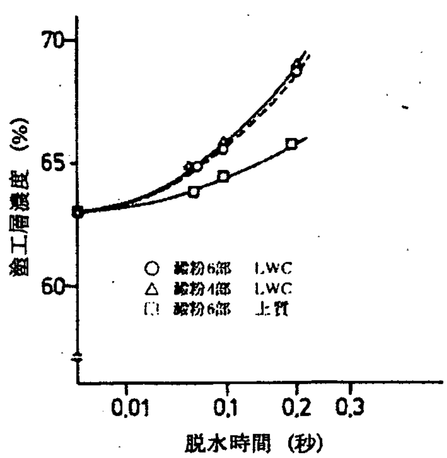

図 24　ブレードコータでの脱水時間と塗工層濃度

ラッチだけでなく，ブリーディング（ブレード先端からの塗料の湧き出し）の原因ともなる。このため，塗料の保水性や原紙バリア性の向上が重要なことや，ブレードに引っ掛かる凝集物や異物をうまく逃がすために原紙に適度な粗さをもたせること，塗料に光沢を害さない程度（12～17部）の重質炭カルを配合することなどが提案された[81]。また，ブレード先端の形状として，ベントブレード（図25[81]右）がベベルブレード（図25左）と比較して，スクラッチの原因となる凝集物を通過させやすいことが報告されている。

ブレードコータの高速化と同様に，オフセット印刷の高速化，多色化が進み，バインダマイグレーションによる印刷モットルが問題となり始めた。バインダマイグレーションの問題が文献に多く現れるの1980年代以降であるが，その現象は古くから知られている。Dappen[82]は澱粉―クレー系塗料で，強乾燥すると澱粉が塗工層表面にマイグレーションし，これがインキ着肉性やピッキングなどに影響すると報告している。バインダマイグレーションは，乾燥条件の影響だけでなく塗料濃度の影響も大きく，低濃度塗料では乾燥条件によって原紙側にも塗工層表面側にも大きくマグレーションする（図26[83]）。このため，バインダマイグレーションを低減するにはできるだけ高濃度で塗工することが好ましく，また，乾燥方法としては，塗料の不動化濃度付近で乾燥を弱めることが良いと報告され[84]，ドライヤを通過している塗料の不動化を検知し，その部分のドライヤ温度，風量を調整する方法が提案された[85]。一方，塗工方法の影響に関して，バインダマイグレーションによる塗工層表面の不均一なバインダ分布は塗工量分布の影響が大きく，凹みを埋めるように塗工するブレードコータが，輪郭塗工となるエアナイフコータと比較して印刷モットルが出易いという報告もある[86]。

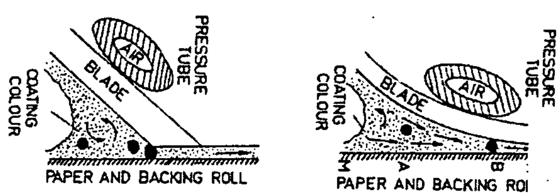

図 25 ブレード先端での粗大粒子の流れ模式（ベベルブレードとベントブレードの差）

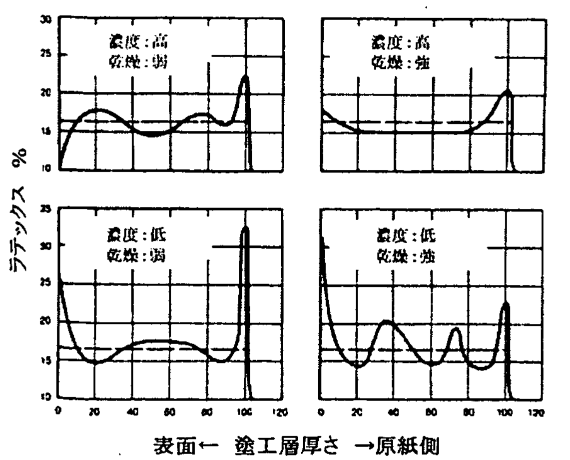

図 26 バインダマイグレーションに対する塗料濃度，乾燥条件の影響

ドライヤについては，フロータドライヤ[87]や赤外線ドライヤ[88]など，両面あるいは内部から乾燥する方法が提案され，バインダマイグレーションを緩和する乾燥方式が導入されたが，1980年代から1990年代前半は，バインダマイグレーションと印刷モットルの研究が多数行われた時期である。

5. 微塗工紙の出現とその急成長（1980年代およびそれ以降）

5.1 微塗工紙とゲートロールコータ

1969年本州製紙富士工場＃6 PMにゲートロールコータ（図27[89]）が設置され，片面当たり塗工量4～5 g/m² のオンマシン顔料塗工が開始された。これが，微塗工紙のスタートとされている[90]。微塗工紙の生産が本格的になったのは1979年頃からであり，非塗工紙と軽量コート紙の間を狙った商品としてオフセット輪転，グラビア輪転の普及に伴うユーザーのコストダウン指向とうまく合致し，出版社からも高い評価を得た。1985年に微塗工紙委員会が発足し，当初印刷用紙Bと印刷用紙Cに含まれていたものを，塗工量12 g/m² 以下を「微塗工紙」とした。その生産量が統計に表れるのは1987年からであるが，軽量コート紙と同様に現在まで高い伸びを続けている（図1/98年に微塗工からA3への一部移行があり，その際の数量減を除く）。その1987年の微塗工紙生産用コータは，ゲートロールコータが11台，ショートドェルコータ

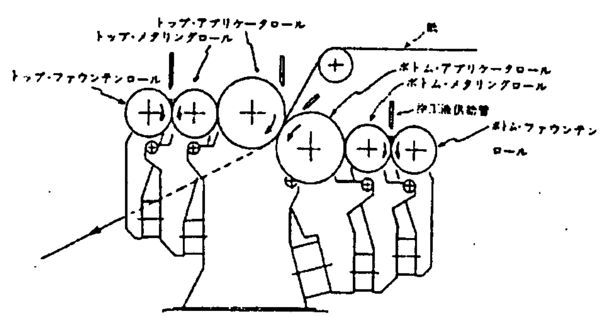

図 27 ゲートロールコータ

(後述) が2台, ビルブレード (図28[91]) が3台, ベルバパコータが2台, オフマシンブレードコータが1台となっており[18], ブレードコータ以外は, 両面同時塗工可能なコータであることが特徴である。

微塗工紙は当初ゲートロール紙とも呼ばれており, この方式での塗工が現在でも多い。ゲートロールコータは, トランスファロールコータの一種で, メタリングロールとファウンテンロールの間に塗工液が供給され, アプリケータロール上に形成した皮膜を紙に転写塗工する方法で, メタリングロール, ファウンテンロールは紙と同速度で回転するアプリケータロールよりゆっくり回転させることができるので, ボンド部での塗工液のボイリングが少ない, 高濃度塗工が可能, 塗工量調整が容易などの特徴がある。ビルブレードコータ, ベルバパコータは, 片面がブレードコータで反対面がロールコータによる塗工であり, 同種のものに, ワルチラ社のツーストリームコータもある。ビルブレードコータは, ブレード側はベントブレード, ロール側はロールを紙より少し速く回転させることでスプリットパターンを軽減している。ベルバパコータは, Sマチックブレードとゲートロールコータの組み合わせであり, ブレードへの塗料供給は, ロールアプリケート, ショートドエルの選択が可能である。

最近では, 特にヨーロッパにおいて, フィルムトランファコータ (図29[92]) を顔料塗工に使用することが広まっており, これらの装置で塗工された紙はフィルムコーテッド紙と呼ばれ, 従来のLWCとSC紙の間に位置するグレードとして認知されている。国内においても1997年頃よりフィルムトランスファコータが微塗工紙の生産に使用されている[93]。

5.2　ゲートロールコータ, フィルムトランスファコータ用の塗料流動特性

ゲートロールコータ, フィルムトランスファコータにおいて, オレンジピールなどパターンの改善, 少量塗工での被覆性改善, 高速化に伴うミスティング発生の防止などが塗料に求められる重要特性である。これらに対し, ニップ部での塗料の不動化層形成度合い (図30[92]), すなわち, ロールから紙への転写率が大きく影響しており, 紙に転写されずにロール上に残る塗料膜厚が大きい程オレンジピールとミスティングが悪化

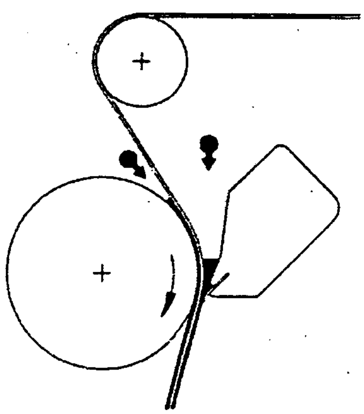

図 28　ビルブレードコータ

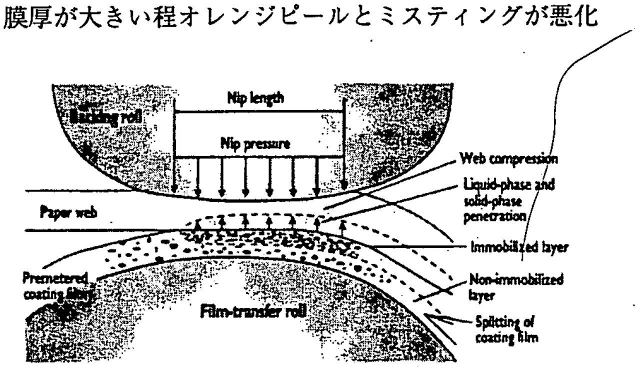

図 30　フィルムトランファコータニップでのフィルタケーキ形成模式図 (片面塗工の場合)

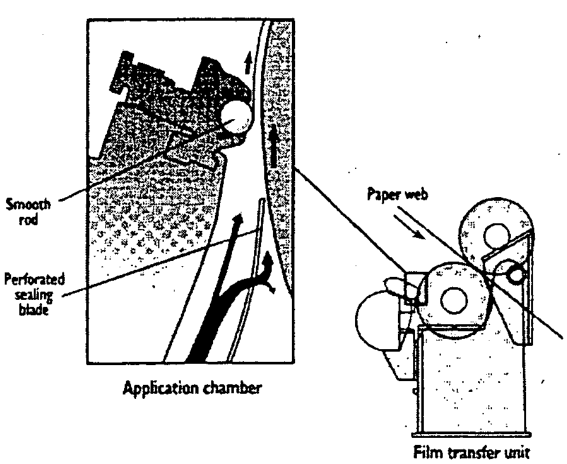

図 29　フィルムトランスファコータ

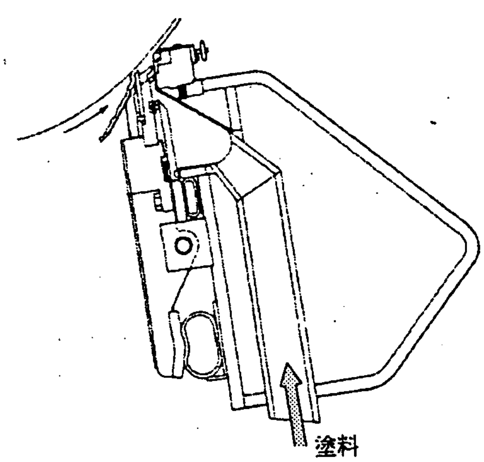

図 31　ショートドエルコータ

する。このため，塗料としては高濃度で保水性の劣る方が好ましく，同時に被覆性も改善されるなど，ブレードコータに求められる塗料特性と異なる点がある。また，原紙や塗料の粘弾性の影響も報告されている[92,94~96]。

5.3　ショートドエルコータ

米国コンソリデーテッド社が基本特許（USP 4,250,211）を有するコータで，塗料供給部とブレードを一体化して，塗料が原紙上に供給されてからブレードで計量されるまでの間隔をできるだけ短くした軽量塗工に適するコータであり，チャンバーアプリケーション方式と呼ばれることもある（図31[97]）。塗料から原紙への水浸透が少ない間にブレードで計量されるので，フラデッドニップなどのロングドエルタイプと比較して，同じ塗工量を得るのにブレード加圧力が低くて済み（図32[98]），薄紙でも紙切れし難いこととが特徴である。1976～1980年の間にコンソリデーテッド社にベロイト社と共同開発したものが導入され，コンソリデーテッド社以外には1982年以降に導入が進み，国内でおいては1985年頃より導入された。

ショートドエルコータは上記メリットを有する反面，1000 m/分程度以上の高速になるとブレードとバッキングロールで形成されるチャンバー内で渦流が発生し（図33[27]），これが原因で原紙への塗料浸透ムラを誘発し，数cm間隔での流れ筋（ウェットストリーク/図34[99]）が発生する。このため，高速時チャンバー内での渦流発生を防止する整流装置などを設けた改良タイプが開発されている[38,99]。また，チャンバー幅をスキップコーティングが出ない程度に小さくすることで改善できるという報告もある[100]。

一方で，塗料を原紙に供給してブレードで計量するまでの間隔（ドエル長さ）が塗工紙品質に影響することも明らかになっており，ショートドエルコータでは塗料がブレードで計量された後も，パルプの膨潤による原紙の荒れや塗料の原紙への浸透が発生し塗工面の平滑劣化が起こり易い。このため，塗料濃度や塗工量に応じてドエル長さを調整できるコータが1980年代半ばに開発された[101]。

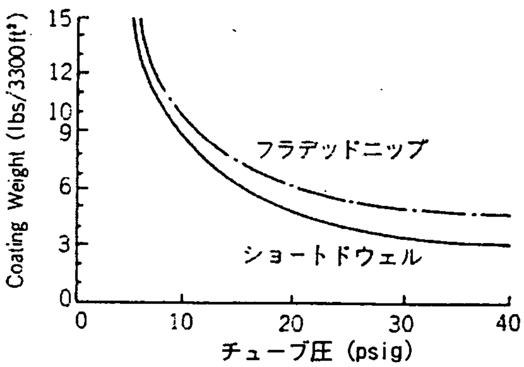

図 32　ブレード加圧力と塗工量の関係（アプリケート方法の差）

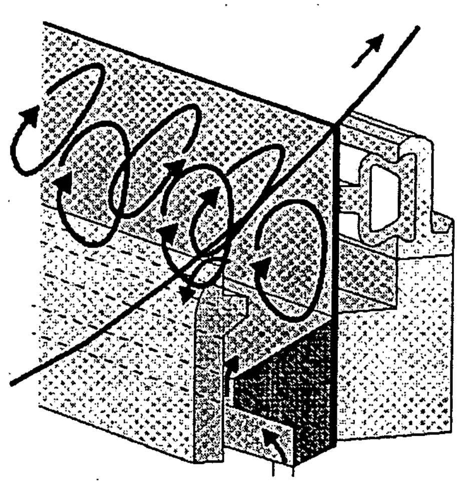

図 33　ショートドエルコータチャンバでの渦流

6.　ブレードダブル塗工による高品質化（1990年代）

6.1　ブレードダブル塗工の効果

微塗工紙や軽量コート紙の伸びとともに，一方では高級塗工紙であるアート紙やコート紙への要望も高い。1970年代後半から1990年代前半の10数年間に，ア

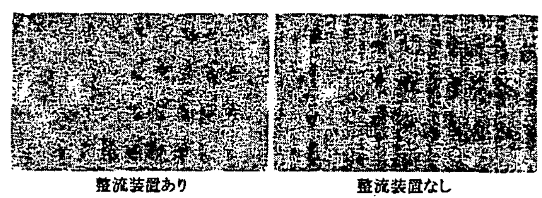

図 34　ショートドエルコータでのウェットストリーク

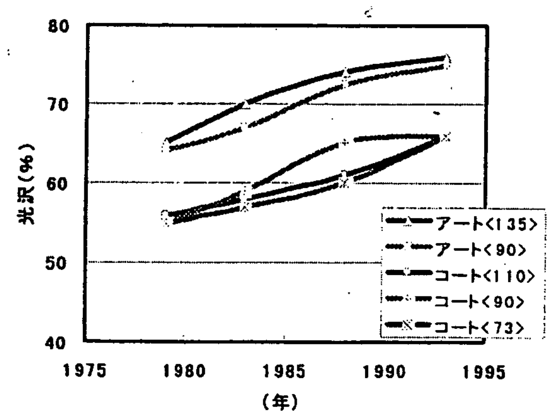

図 35　アート紙，コート紙の光沢推移（1979～1993年）

ート紙とコート紙でそれぞれ約10ポイントの光沢向上が図られている（図35[22]）。これを成し得たのは，微粒カオリン，各種形状の微粒軽質炭酸カルシウム，中空で代表される各種プラスチックピグメントなど光沢発現性の高い顔料の導入による塗料処方面での改良効果も大きいが，ブレードダブル塗工の効果を無視することはできない。ちなみに，弊社調査では，1990年代前半から現在までにコート紙においては，光沢がさらに10ポイント程度上積みされており，今やコート紙の光沢は，アート紙（A1グレード）と同等レベルに達している。

ダブル塗工は決して新しいものでなく，国内においてはロールコータ＋チャンプレックスコータの組み合わせで始まり，ロッド＋エアナイフ，ロール＋ブレード，ブレード＋エアナイフなど各種の組み合わせが板紙を含めて実施されてきた。これは，紙塗工が(A)原紙の細孔や凹凸を埋めて平滑化する作用と(B)原紙を水で濡らすことで原紙凹凸を大きくする作用の両方を同時に行っており，この相反する作用で(A)の効果だけを得るための手法がダブル塗工であり，現時点で最も高い平滑性が得られる塗工方法の組合わせで実施しているのがブレードダブル塗工である。ブレードダブル塗工を1パスで可能とするいわゆる4ヘッドのブレードコータは1989年に改造された王子製紙米子工場の#4CMが最初で，アート紙が製造された。その後，王子製紙春日井工場の#3CM（1991年），十条製紙石巻工場の#2CM（1991年）と続く。

ダブル塗工の効果は，上記した機構による平滑性，白紙光沢や印刷光沢改善の他に，ブレードコータの高速化の項で述べた印刷モットルに対しても，1層当たりの塗工量が少なくなることや塗工量の均一性が増すことにより乾燥条件や塗料処方の許容範囲が大きくなるメリットがある[102,103]。また，コスト面でも下塗りを安価な処方とすることができるので有利である。

6.2　ジェットファウンテンコータ

ダブル塗工とは直接関係はないが，1980年代後半からの特徴ある技術としてジェットファウンテンアプリケータ（フリージェットアプリケータとも呼ばれる）を外すことはできない。ジェットファウンテンアプリケータは，0.5〜1 mmの隙間を持つスリットノズルから塗料を原紙に吹き付けて供給する方法であり（図36[27]），国内では1980年代後半より，欧米では1990年代半ばより採用され，現在では主流の塗料供給方法となっている（図37[24]）。その機構については，多数の紹介があるので省略するが[101,104〜106]，ファウンテンの吹き出し角度などの最適化と効率の良い脱泡機との組み合わせにより，バックフローなしでスキップコー

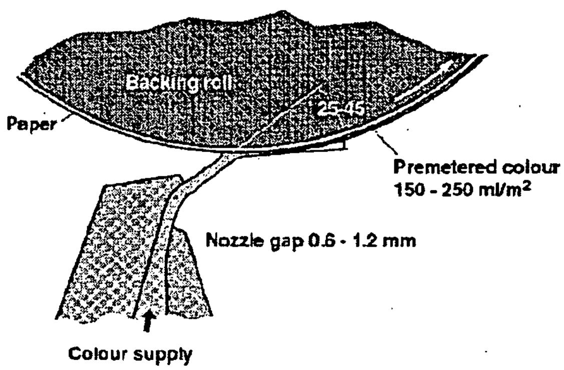

図36　ジェットファウンテンアプリケータ

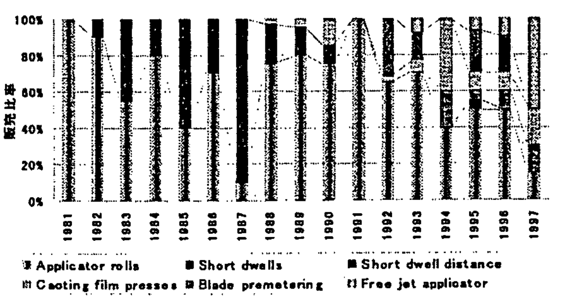

図37　ヨーロッパ，米国でのコータヘッド販売シェア推移

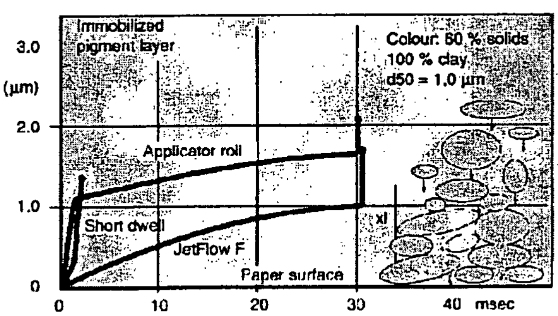

図38　アプリケート方法とフィルタケーキ層厚さ

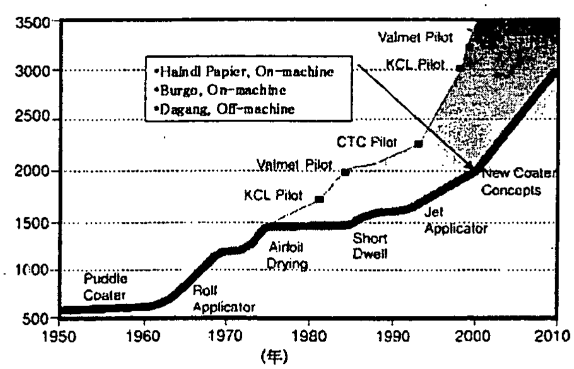

図39　実機とパイロット機のコータ速度推移と予測

ティングを防止できる。また，フラデッドニップアプリケータで問題となったブレードで塗料が掻き落されるまでの間における過剰なフィルターケーキの形成を防ぎ，高濃度塗料を高速でしかもブレードに大きな負荷をかけることなく塗工できることが特徴である（図38[27]）。

7. おわりに

コータの速度（設計速度）は，1999年には2,000 m/分の大台に入り，すでにパイロットコータでは3,000 m/分以上の速度領域となっている。このことから，早ければ2010年には3,000 m/分の時代が来ると予想されている（図39[39]）。このような高速塗工は，コータだけでなく，これに絶えうる原紙と良好な塗工適性を有する塗料が組み合わさってなし得るものであり，顧客の求める品質と高い生産性をバランスさせるには，これまで以上に塗料処方の重要性が高まるものと思われる。一方で，今年Metso　Paper社よりスプレーコーティング[107]が紹介され，カーテンコーティング[108]とともに，次の印刷用塗工紙の高速塗工技術となり得るのか当事者として非常に興味がある。

最後に，今回紙面の都合でキャスト紙や塗工紙製造におけるカレンダー技術に触れることができなかったことをお詫びするとともに，本内容が紙塗工に携わる方々に何らかの参考になれば幸いである。

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